CATALYTIC GENERATION OF HYDROGEN AND CHEMICALS FROM BIOMASS DERIVED POLYOLS

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The principal goal of this research is to produce hydrogen from biosustainable polyols, compounds containing a hydrocarbon chain with neighboring hydroxyl groups, such as glycerol or sorbitol.

Hydrogen is an energy carrier which can replace oil and reduce pollution and greenhouse gas emissions when it is generated from renewable sources. At present, hydrogen is derived from fossil fuels such as natural gas, naphtha or coal. We show that hydrogen can be produced by reforming of glycerol, sorbitol, glucose or sucrose in water at a low temperature (e.g. 200^{o}C) over supported metal catalysts. A thermodynamic analysis that forms the basis of the process compares aqueous phase reforming of polyols with steam reforming of alkanes. Catalyst screening involving different noble metals and different supports indicates that alumina supported platinum catalysts are effective for hydrogen production by aqueous phase reforming of polyols. In an attempt to achieve high hydrogen yields, the effects of operating temperature, pressure, and nature of the feed are studied. Higher operation temperatures favor higher hydrogen yields while hydrogen production is strongly inhibited by high system pressure. Short chain polyols have better hydrogen selectivities than long chain polyols.

An effort is made to show that valuable chemicals can be derived from polyols. Glycerol and other polyols are potential sources of value-added chemicals, such as 1,2-propanediol, a major commodity chemical now obtained from petroleum derived propylene. It can be generated by an alternative renewable route through hydrogenolysis of biodiesel-derived glycerol. The effects of hydrogenolysis conditions such as reaction temperature, hydrogen pressure, water content in the feed and catalysts are evaluated. Both high temperature and high hydrogen pressure favor 1,2-propanediol formation.

This research discusses biorefinery processes and shows how biosustainable polyols can be used as a source of hydrogen and of chemicals. The development of the aqueous phase reforming of polyols to produce hydrogen and the hydrogenolysis of polyols to generate value-added chemicals build a foundation for further research.

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1.0 INTRODUCTION

Global energy consumption is expected to increase dramatically in the next decades, driven by rising standards of living and a growing population worldwide. At present, world energy needs are largely met by use of fossil fuels, chiefly oil, natural gas and coal. There is a rising consciousness that we may not be able to depend on petroleum as the principal source of fuels and of chemicals in the coming decades. The limited amounts of fossil fuels, especially petroleum, and concurrent environmental problems such as greenhouse gases, have prompted the world to look for clean sustainable resources as alternatives to meet increasing energy demands. Biomass has the potential to meet a portion of the challenges of sustainable and green energy systems.

Biomass is any organic material made from plants or animals. Domestic biomass resources include agricultural and forestry residues, municipal solid wastes, industrial wastes, and terrestrial and aquatic crops grown solely for energy purposes. Biomass is a sustainable feedstock for energy products that could potentially substitute for fossil resources for power, fuels and chemicals. Environmental, economic and energy conservation aspects drive us towards greater use of the biosustainable resources, known as biorefinery.

Biorefinery is a term analogous to an oil refinery system. A biorefinery processes biomass into value-added product streams. Figure 1 illustrates the biorefinery system and its product slates [1]. Biomass is a source for fuels and energy, materials and chemicals. The

products range from biomaterials to fuels such as ethanol, biodiesel and fuel gases, or key intermediates for the production of chemicals and other materials.

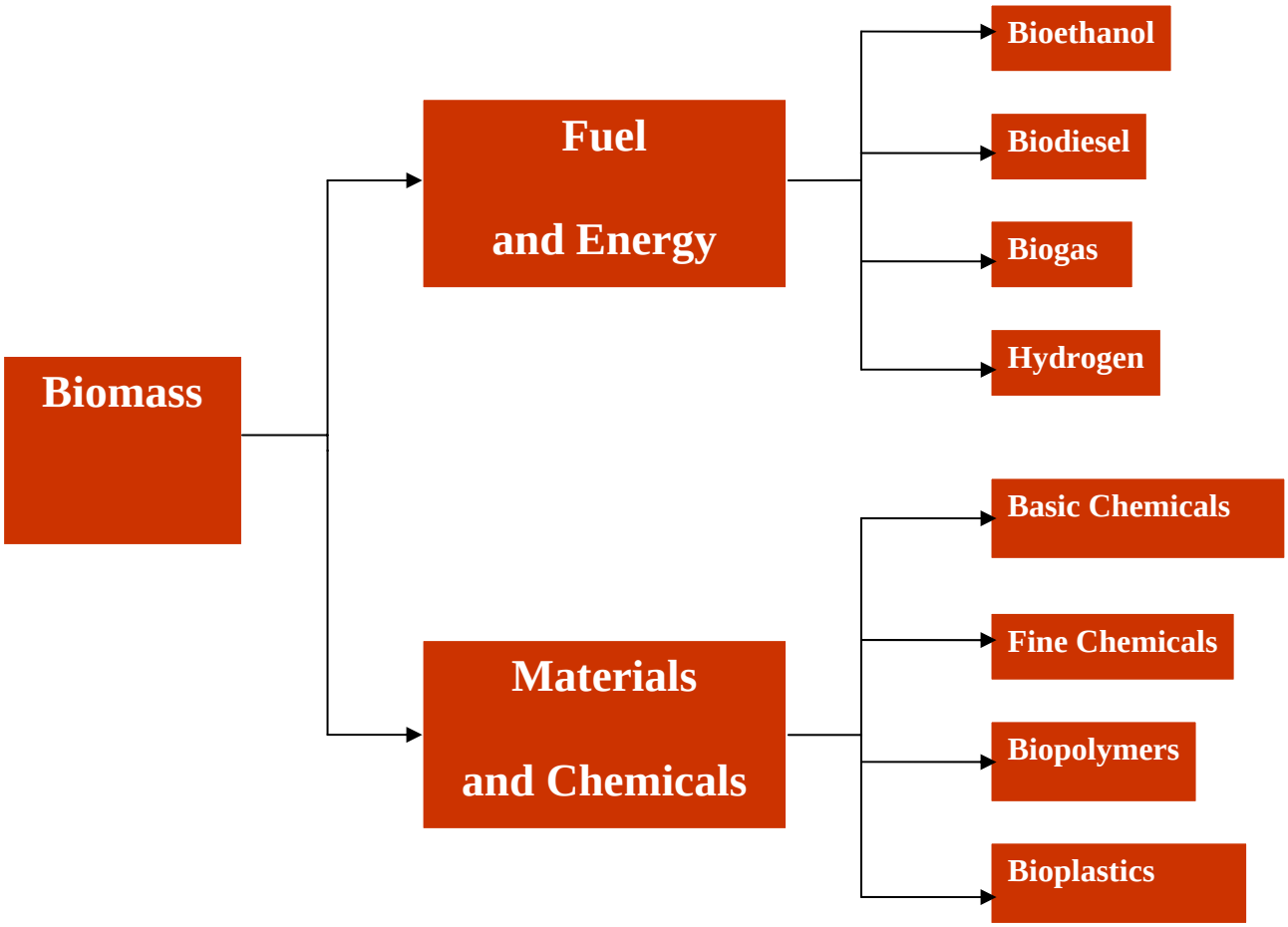


Figure 1. Biomass routes to fuels and chemicals

Biorefineries are based on a number of processing platforms (e.g. sugar platform and synthesis gas platform) using mechanical, thermal, chemical, and biochemical processes. The

sugar platform converts biomass into its component sugar molecules by hydrolysis and then ferments the sugars into energy products; the synthesis gas platform breaks down biomass into carbon monoxide and hydrogen, and then uses basic chemistry to convert these elements into energy products.

The U.S. Department of Energy and the Department of Agriculture in 2003 estimated that roughly 2 billion dry tons of biomass is produced annually in the U.S. in the form of crop, forest, mill residues, livestock and municipal wastes. Forest residues produced from traditional forest product industries have and will continue to produce about 200 million dry tons of forest residue biomass per year. This biomass resource is the primary source of bioenergy today [1].

Biomass feedstocks currently supply about 3×10^{15} BTUs (British thermal unit, 1 BTU is the amount of heat required to raise the temperature of one pound of water by one degree Fahrenheit) to the nation's energy supply based primarily on wood resources; it is expected to increase to 10^{16} BTUs in the near future [2]. Biomass was estimated to be the source of 47% of all renewable energy or 4% of the total energy consumed in the U.S. in 2007 [3]. Current biomass consumption in the U.S. is dominated by industrial use, largely derived from wood. The U.S. Energy Policy Act of 2005 [4] called for biomass consumption in the industrial sector to increase at an annual rate of 2% through 2030, increasing from 2.7 quads in 2001 to 3.2 quads in 2010, 3.9 quads in 2020, and 4.8 quads in 2030 (A quad is a unit of energy equal to 10^{15} BTU, or 1.055×10^{18} joules). Moreover, biomass consumption in electric utilities will double every 10 years through 2030. Biopower will meet 4% of total industrial and electrical generator energy demand in 2010 and 5% in 2020 [1]. Transportation fuels from biomass [1] will increase significantly from 0.5% of U.S. transportation fuel consumption in 2001 (0.147 quads) to 4% of transportation fuels consumption in 2010 (1.3 quads), 10% in 2020 (4.0 quads), and 20% in

2030. Production of chemicals and materials from biobased products will increase substantially from approximately 12.5 billion pounds, or 5% of the current production of target U.S. chemical commodities in 2001, to 12% in 2010, 18% in 2020, and 25% in 2030 [1]. The remarkable growth in efforts to utilize biomass as a source of both fuels and chemicals, heretofore derived from petroleum, makes it seem likely that these quantities will be easily surpassed. However, it is important to keep these numbers in perspective; in 2004, for instance, the U.S. consumed 140 billion gallons of gasoline and about 40 billion gallons of diesel as transportation fuels [2]. Increased use of biofuels is not a panacea but should be viewed as one of a possible range of measures aimed at reducing our dependence on fossil fuels. Biofuels are carbon dioxide neutral which helps in alleviating climate change problems.

The past few years have seen a remarkable increase in efforts to utilize biomass as a renewable source of fuels and chemicals. Ethanol and biodiesel, made from plant matter instead of petroleum, can be blended with or directly substituted for gasoline and diesel, respectively. The benefits of the use of biofuels are reduction of toxic air emissions, while decreasing our dependence on imported oil. Carbon dioxide released from burning biofuels is balanced by the carbon dioxide capture by the growth of the plant materials from which they are made, resulting in reduction of greenhouse gas emissions. Use of liquid transportation fuels such as ethanol and biodiesel is increasing dramatically in recent years. The U.S. ethanol industry produced more than 3.4 billion gallons in 2004, up from 2.8 billion gallons in 2003 and 2.1 billion gallons in 2002 [5]. According to the National Biodiesel Board, the U.S. biodiesel demand has increased from 15 million gallons in 2002, to 75 million gallons in 2005, and to 225 million gallons in 2006, an increase of 15 times in 4 years [6].

There are still concerns and debate related to how useful bioethanol will be in replacing fossil fuels in vehicles [7]. For bioethanol, the concerns relate to the large amount of arable land required for crops [8], as well as the energy and pollution balance of the whole cycle of ethanol production [9]. For biodiesel, the concerns relate to deforestation of tens of millions of acres of forest in order to grow oil producing plants, such as palm oil, especially in the Philippines and in Indonesia. Both countries plan to increase their biodiesel production levels significantly, which will lead to significant deforestation if these plans materialize [9]. Another concern comes from the process of biodiesel production. The increasing production of biodiesel has resulted in a glut of glycerol, a by-product of biodiesel production; its price has dropped by two-thirds in the last 5 years. The surge of biodiesel production will yield an additional 1 billion lbs of glycerol over the next two years [10]. One attractive possibility is to use this cheap and available glycerol for the production of hydrogen and value-added chemicals, such as propylene glycol. Our work will include a variety of polyols, but we have used glycerol as a model compound for conversion of a polyol to hydrogen (and later to chemicals).

Hydrogen has the potential to solve two major energy challenges that confront America today: reducing dependence on petroleum imports and reducing pollution and greenhouse gas emissions. There is a growing interest in replacing fossil fuels with hydrogen in a so-called hydrogen economy, a future economy in which energy for transportation and power is stored as hydrogen. Hydrogen was first discovered by Henry Cavendish in 1766 and then named by Antoine Lavoisier in 1783; its meaning is derived from the generation of water when it burns. Hydrogen has fascinated generations of people for centuries. In the 1870s, Jules Verne predicted with impressive foresight the use of hydrogen as fuel in his classic book Mysterious Island [11]. Rudolf Erren began designing hydrogen engines in the 1930s and suggested using hydrogen as a

transportation fuel to reduce oil imports [12]. Hydrogen was used to supplement fuel in large dirigibles in both Germany and England before the Hindenburg disaster on May 6, 1937. Nowadays, most hydrogen is used as a chemical, rather than a fuel, in a variety of applications, such as ammonia production, fossil fuel processing, methanol production and hydrogenation of fats and oils. Hydrogen's main use as a fuel is in the space program, where hydrogen fuels both the main engine and onboard fuel cells. The possibility of using hydrogen as a general energy carrier has long been recognized[13-15]. The Department of Energy has been a strong proponent for research and development related to hydrogen energy development in the U.S., setting a goal for hydrogen to provide 10 percent of the nation's energy needs by 2030 [16]. The January 2003 announcement by President Bush of the Hydrogen Fuel Initiative stimulated the interest of both the technical community and the broader public in the "Hydrogen Economy" [17].

The elements involved in this new complex system include hydrogen production, storage and transmission, as well as use of hydrogen for fuel or for fuel cells. The transition to a hydrogen economy could take several decades and could occur through a series of phases. Hydrogen based on current technologies is first being used in those areas where the required modification in infrastructure is modest, such as fuel cell buses with filling stations. With new technologies in hydrogen production and market expansion, the present price for producing hydrogen is expected to decline. Then breakthroughs in methods of hydrogen storage would have a significant impact on hydrogen usage. Finally improvements in fuel cell manufacture, performance and durability would allow hydrogen to become a major energy carrier.

Although hydrogen is the most abundant element in the universe, free hydrogen does not exist naturally on earth in its gaseous form. Hydrogen is not an energy source but an energy carrier since it must be produced from a primary source such as water, natural gas, coal,

petroleum or biomass. The development of clean, sustainable, and cost-competitive hydrogen production processes is a key to a viable future hydrogen economy.

Today, nearly all hydrogen production is based on fossil raw materials. Hydrogen is a global commodity with 50 million tons of hydrogen produced every year around the world. In 2004, worldwide, 48% of hydrogen was produced from natural gas, 30% from oil, 18% from coal, and the remaining 4% via water electrolysis [18]. The U.S. demand for hydrogen currently is about 9 million tons per year. Approximately 95 percent of hydrogen is currently produced via steam reforming [18], a thermal process typically carried out over a nickel-based catalyst, which involves reacting natural gas or other light hydrocarbons with steam. This is a three-step process that results in a mixture of hydrogen and carbon dioxide, which is then separated by pressure swing adsorption to produce pure hydrogen. Steam reforming is a cost-effective means of producing hydrogen but probably not a viable way to energize a hydrogen economy. The available supply of natural gas is not adequate to support our growing need to use it for generating electricity, heating our homes and meeting hydrogen demands of industry. One downside to steam reforming is the amount of carbon dioxide, the main greenhouse gas, generated when hydrogen is produced in this way.

A full environmental benefit of generating power from hydrogen can be achieved only when it is produced from renewable sources such as solar power or biomass; in the latter case, CO_2 produced as a byproduct can be fixed and consumed during the growth of plants used for further hydrogen production. Nature has also provided us with a vast resource of sugars and sugar alcohols. Starches and cellulose are both composed of glucose polymers; hemicelluloses are composed of four or five carbon entities. All have adjacent hydroxyl groups on a

hydrocarbon chain and are included under the term, polyols. It is the intent of this research to show how polyols can be used as a source of hydrogen and of chemicals.

Our work started in 2003, based on the discovery by Professor Dumesic and his group at University of Wisconsin that significant amounts of hydrogen can be obtained by aqueous phase reforming of ethylene glycol, glucose and sorbitol [39]. Their initial paper was published in Nature in August 29, 2002. Dumesic's work was an inspiration to me and opened the field for me to explore. We started working with similar substances and extended our work to mannitol, sucrose, table sugar and corn syrup. We focused largely on glycerol, a byproduct of biodiesel manufacture. My research not only focuses on obtaining hydrogen as a fuel from biomass-derived polyols, but also explores the possibilities of getting value-added chemicals from those polyols. It is our intent to integrate those two processes together to address the goals of biorefinery on both energy and economic sides.

The next chapter gives a review of hydrogen production technologies. It covers thermal processing, electrochemical and biological processing, from the steam reforming of natural gas, to coal and biomass gasification, to high temperature water splitting and biological hydrogen production. It emphasizes the aqueous-phase reforming (APR) process to produce hydrogen. Aqueous phase reforming of polyols to produce hydrogen greatly reduces energy consumption by controlling the reaction in liquid phase, leading to lower operation temperature, compared with the energy extensive steam reforming of natural gas for hydrogen production. By using the biomass-derived polyols, APR helps to realize environmental benefit of reduction of greenhouse gas emission. Experimental procedures for aqueous phase reforming are described in Chapter 3. A discussion of thermodynamic and experimental results is presented in Chapters 4 and 5. We show why APR of polyols for hydrogen production can be operated at low temperatures (around

200^{o}C) and can achieve low formation of carbon monoxide (less than 500 ppm). This work also includes production of valuable commodity chemicals from hydrogenolysis of polyols, presented in Chapter 6. Polyols can be the sources for many valuable fine chemicals; hydrogenolysis provides us a means to utilize hydrogen from the APR and gives us an alternative route to produce chemicals from renewable sources.

2.0 BACKGROUND

2.1 HYDROGEN GENERATION

Hydrogen can be produced using diverse resources including fossil fuels, nuclear, biomass and other renewable energy technologies, such as wind and solar. It is expected and desirable for hydrogen to be produced using a variety of resources and technologies. This diversity of domestic energy sources makes hydrogen a promising energy carrier and can strengthen national energy security. Currently, hydrogen can be produced by thermal processes (natural gas steam reforming, coal and biomass gasification, biomass pyrolysis and bio-oil processing), electrochemical processes (water splitting using a variety of energy resources), and biological processes (splitting water using sunlight via biological and electrochemical materials), as shown in Table 1.

Table 1. Primary methods for hydrogen production [19]

Primary Method	Process	Feed Stock	Energy	Emissions
Thermal	Steam Reforming	Natural Gas	High temperature steam	Some emissions, carbon sequestration may reduce the effect
	Thermochemical Water Splitting	Water	High temperature heat from advanced gas-cooled nuclear reactors	No emissions
	Gasification	Coal, Biomass	Steam and oxygen at high temperature and pressure	Some emissions, carbon sequestration may reduce the effect
	Pyrolysis	Biomass	Moderately high temperature steam	Some emissions, carbon sequestration may reduce the effect
Electrochemical	Electrolysis	Water	Electricity from renewable energy (wind, solar, hydro and nuclear)	No emissions
	Electrolysis	Water	Electricity from coal or natural gas	Some emissions from electricity productions
	Photoelectrochemical	Water	Direct sunlight	No emissions
Biological	Photobiological	Water and algae	Direct sunlight	No emissions
	Anaerobic Digestion	Biomass	High temperature heat	Some emissions
	Fermentative Microorganisms	Biomass	High temperature heat	Some emissions

2.1.1 Steam reforming

Current industrial hydrogen production starts from steam reforming of methane. Methane reacts with high temperature steam (700~1000^{o}C) under 3-25 bar pressure in the presence of a catalyst to produce a mixture of hydrogen, carbon monoxide, and a relatively small amount of carbon dioxide. The reaction is strongly endothermic; heat must be supplied for the reaction to proceed.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H_1 = -252.3 \text{ kJ mol}^{-1} \qquad (2.1)$$

In order to obtain high conversions of methane and high selectivity to hydrogen, the steam reforming reaction is followed by a subsequent water-gas shift reaction, where the carbon monoxide and steam are reacted in the presence of a catalyst to produce carbon dioxide and more hydrogen.

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H_2 = 41.1 \text{ kJ mol}^{-1} \qquad (2.2)$$

Heat is recovered and recycled back to the first reaction. Industrial steam reformers usually use direct combustion of a fraction of methane to supply heat for the process (2.1)

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H_3 = 894.7 \text{ kJ/mol} \qquad (2.3)$$

Typical steam/methane ratios are 2 to 3, which is above the stoichiometric reaction ratio to avoid char formation and excess CO formation [20]. The catalysts for this reaction are nickel or nickel, cobalt, alkali and rare earth mixtures. New catalysts for hydrogen production have been tested and brought into use, from the traditional Ni/Al_2O_3 [21] to Ni/ZrO_2 [22] to a new Ni/Ce-ZrO2 catalyst [23]; the latter yields 15% more hydrogen than the traditional catalysts.

The shift reaction uses an additional set of catalysts, typically Fe or Cr oxides, employed in the first step at around 400^{o}C; in the second step, a low temperature shift reaction, $Cu/ZnO/Al_2O_3$ catalysts are used.

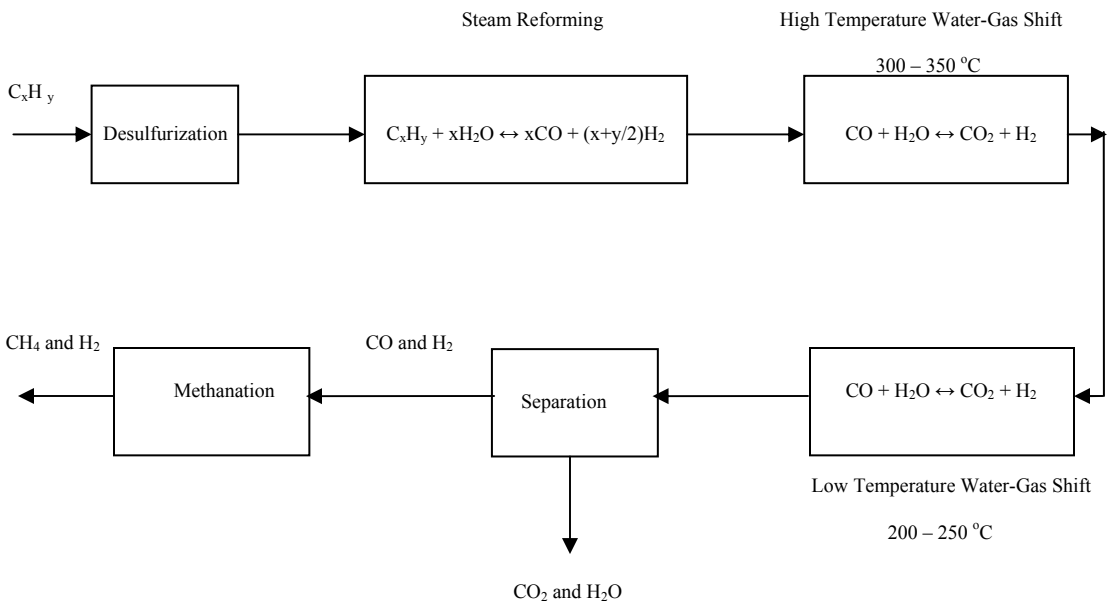


Figure 2. Current multistep generation of hydrogen from hydrocarbons [24]

The total process is complicated and energy intensive; it includes desulfurization, steam reforming, water-gas shift, methanation, as well as water and carbon dioxide separation. Current natural gas steam reforming in industrial plants is not aimed at fuel cell use of the hydrogen; the carbon monoxide remaining after the shift reaction is in the range of 0.3 ~ 3% [25, 26]. Such amounts of carbon monoxide act as a poison for low temperature PEM fuel cells and thus must be removed. Complex and expensive multiple processes must be used to achieve low carbon monoxide levels to make hydrogen suitable for use in fuel cells. The carbon monoxide cleaning process may involve preferential oxidation, methanantion or membrane separation [25]

2.1.2 Partial oxidation, autothermal reforming and dry reforming

Natural gas partial oxidation is another common method for hydrogen production. The methane and other hydrocarbons in natural gas are reacted with a limited amount of oxygen, not enough to completely oxidize the hydrocarbons to carbon dioxide and water. With less than the stoichiometric amount of oxygen available for the reaction, the reaction products contain primarily hydrogen and carbon monoxide, as well as relatively small amounts of carbon dioxide and other compounds.

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \qquad \Delta H_4 = 35.7 \text{ kJ/mol} \qquad (2.4)$$

Full oxidation (2.3) and product oxidation (2.5, 2.6) also occur to a small degree in the process.

$$CO + 1/2O_2 \rightarrow CO_2 \qquad \Delta H_5 = 280.3 \text{ kJ/mol} \qquad (2.5)$$

$$H_2 + 1/2O_2 \rightarrow H_2O \qquad \Delta H_6 = 288 \text{ kJ/mol} \qquad (2.6)$$

Subsequently, in a water-gas shift reaction, the carbon monoxide reacts with water to form carbon dioxide and more hydrogen. Nickel catalyst (Ni/SiO_2) is a typical catalyst for partial oxidation. Partial oxidation is an exothermic process that is more rapid than steam reforming and requires a smaller reactor vessel. The method is suitable for small scale hydrogen production, such as serving as a hydrogen reformer for fuel cells. However, this process initially produces less hydrogen per unit of input fuel than is obtained by steam reforming of the same fuel. Partial oxidation can serve as an initial step to provide heat for the high temperature needed for starting steam reforming. This is called autothermal reforming, which involves all the reactions mentioned above. Hydrogen production by partial oxidation of methane increases with process temperature, reaching a plateau at around 700^{o}C [27]. The efficiency is close to that of steam reforming, while less water is required [28].

Methane can be reformed in carbon dioxide rather than by steam, which is called dry reforming. Carbon monoxide could be removed by following with the water gas shift reaction.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H_7 = 247.3 \text{ kJ/mol} \qquad (2.7)$$

Dry reforming reactions can operate at relatively low temperatures (e.g. 550^{o}C), consuming carbon dioxide in the reforming [29]. It can be used in combination with conventional steam reforming in fluidized bed membrane reactors [30]. The membrane and reaction coupling could help achieve complete conversion of methane at low temperatures.

2.1.3 Gasification of coal, biomass and pyrolysis of biomass

Gasification is seen as a key pathway to hydrogen when starting from coal or lignin containing biomass, such as wood, wood scraps or other plant material. Coal is an abundant and fairly inexpensive domestic resource. Chemically, coal is a complex and highly variable substance. The carbon and hydrogen in coal may be represented in an approximate manner as 0.8 atoms of hydrogen per atom of carbon in bituminous coal. For agricultural biomass, such as crop residues and forest residues, the carbon is initially contained in a range of sugar-like compounds, such as starch and cellulose. Production of hydrogen from coal or from biomass requires an initial step of high temperature gasification, in which coal or biomass is heated with high temperature steam and converted into a gaseous mixture of hydrogen, carbon monoxide, carbon dioxide, and other compounds under pressure in the presence of a controlled amount of oxygen in the gasifier.

Both coal and biomass are chemically broken apart by the heat, steam, and oxygen in the gasifier and converted to synthesis gas (carbon monoxide and hydrogen). The gasification takes place at temperatures above 900^{o}C in the absence of a catalyst. With a catalyst, the temperature

can be brought down to 700°C [31]. The carbon monoxide is reacted (in a separate unit) with water to form carbon dioxide and more hydrogen, which is then separated from the gas stream.

Coal and biomass gasification technology is most appropriate for large-scale, centralized hydrogen production due to the nature of handling large amounts of coal and of biomass, and the carbon capture and sequestration technologies that must accompany the process together with the required economy of scale. An advantage of gasification technology is that it could be used to generate both electricity and hydrogen in an integrated plant operation, called Integrated Gasification Combined Cycle (IGCC). The plant is called "integrated" because its syngas is produced in a gasification unit in the plant which has been optimized for the plant's combined cycle. The gasification process produces heat, and this is reclaimed by steam used in turbines to produce electricity. However, the future of this process depends on the success of carbon dioxide sequestration. If carbon dioxide can be successfully sequestered and stored, hydrogen can be produced from coal or biomass gasification with near-zero greenhouse gas emissions.

Pyrolysis is the gasification of biomass in the absence of air or oxygen or in the presence of very small amounts of oxygen. In many industrial applications the process is carried out under pressure and at operating temperatures above 430°C, so called anhydrous pyrolysis. The most common technique uses very low residence times (<2 seconds) and high heating rates using a temperature between 350-500°C and is called flash pyrolysis [32]. The ratio of oxygen available and the amount of oxygen that would allow complete burning is called the “equivalence ratio”. For equivalence ratios less than 0.1, the process is called “pyrolysis”, and only a modest fraction of the biomass energy is found in the gas product, with the rest being in char and oil residues. If the equivalence ratio is between 0.2 and 0.4, the process is called “gasification”. This is the region of maximum energy transfer to the gas [32]. In general,

biomass does not gasify as easily as coal, and it produces other hydrocarbon compounds in the gas mixture and liquid fuel similar to diesel, especially when no oxygen is used [32].

As a result, typically an extra step must be taken to reform these hydrocarbons with a catalyst to yield a clean syngas mixture of hydrogen and carbon monoxide. Then, just as in the gasification process for hydrogen production, a shift reaction step (with steam) converts the carbon monoxide to carbon dioxide. The hydrogen produced is then separated and purified.

2.1.4 Renewable liquid fuels reforming

In the U.S. at present there is more available biomass than is required for food and animal feed needs. It is estimated that 1.2 billion dry tons of biomass could be available for energy use by 2050 [33, 34]. Biomass resources can be converted to ethanol, bio-oils, or other liquid fuels that can be easily transported and reformed to produce hydrogen. Ethanol can be made by converting the starch in corn into sugars and fermenting the sugar to produce ethanol [34]. Sugars can also be extracted from other biomass resources, such as crops or forest residues, through a series of steps involving mild acid or steam and enzyme digestion. These sugars are then fermented, producing ethanol [34]. Bio-oils are oil-like liquids which are obtained from pyrolysis of biomass.

Reforming of renewable liquids to hydrogen is similar to reforming of natural gas. Biomass-derived liquids can be produced in large amounts near the biomass source to obtain economies of scale. The liquids can also be easily transported to sites for reforming to hydrogen. Another advantage for this technology is the reduction of greenhouse emissions. Because biomass resources consume carbon dioxide in the atmosphere as part of their natural growth

process, producing hydrogen through biomass gasification releases near-zero net greenhouse gases.

This technology is a new and additional method to produce hydrogen while benefiting agriculture and other industries. It is anticipated that distributed reforming of biomass-derived liquid fuels could be commercial during the transition to hydrogen and used in mid and long-term time frames [33].

2.1.5 High temperature water splitting

High-temperature water splitting is a thermal decomposition of water to produce hydrogen. As the direct thermal decomposition water requires temperature exceeding 2700^{o}C, not possible with presently available materials, attempts have been made to bring the temperature down to below 800^{o}C by indirect routes using catalysts and cyclic chemical processes. The high-temperature heat needed can be supplied by nuclear reactors (up to about 1000°C) or by using sunlight with solar concentrators (up to about 2000°C) [35].

An example of cyclic chemical process is the sulfur-iodine cycle [36, 37]. Sulfuric acid, when heated to about 850°C, decomposes to water, oxygen, and sulfur dioxide. The oxygen is removed, the sulfur dioxide and water are cooled, and the sulfur dioxide reacts with water and iodine to form sulfuric acid and hydrogen iodide. The sulfuric acid is separated and removed, and the hydrogen iodide is heated to 300°C, where it breaks down into hydrogen and iodine.

$$2H_2SO_4 \xrightarrow{850^{o}C} 2H_2O + 2SO_2 + O_2 \quad (2.8)$$

$$2H_2O + SO_2 + I_2 \xrightarrow{120^{o}C} H_2SO_4 + 2HI \quad (2.9)$$

$$4HI \xrightarrow{300^{o}C} 2I_2 + 2H_2 \quad (2.10)$$

The net result is hydrogen and oxygen, produced from water. The hydrogen can be separated and purified. The sulfuric acid and iodine are recycled and used to repeat the process. Solar and nuclear-driven high-temperature thermochemical water splitting cycles produce hydrogen with near-zero greenhouse gas emissions, using water and either sunlight or nuclear energy.

2.1.6 Water electrolysis

Water electrolysis is a well-known process for the production of hydrogen. However, if the electricity needed is produced by use of fossil fuels, then the cost of hydrogen is higher than it is from steam reforming of natural gas. On the other hand, high purity hydrogen needed in some occasions (for fuel cells) is easier to achieve by this technology [35].

This reaction takes place in a unit called an electrolyzer, an anode and a cathode separated by an electrolyte. Water reacts at the anode to form oxygen and protons.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (2.11)$$

The electrons flow through an external circuit and the hydrogen ions selectively move across the PEM to the cathode. At the cathode, hydrogen ions combine with electrons from the external circuit to form hydrogen gas.

$$4H^+ + 4e^- \rightarrow 2H_2 \quad (2.12)$$

The overall reaction is

$$2H_2O \rightarrow 2H_2 + O_2 \qquad \Delta H = 288 \text{ kJ/mol (l)} \quad (2.13)$$

Hydrogen produced via electrolysis can result in zero greenhouse gas emissions, depending on the source of the electricity used. At present, it is not ideal for providing hydrogen on a large scale because of the energy-intensive nature of the electricity generation technologies and resulting greenhouse gas emissions. Electricity generation using renewable or nuclear energy technologies is a possible option for hydrogen production via electrolysis [35].

2.1.7 Biological hydrogen production

Production of hydrogen from biomass may be achieved by biological fermentation or by other bacterial or algae decomposition of water [38]. The conversion processes may proceed in the dark or with light. Growing the biological substance requires an energy input, such as sunlight and heat. Water and sugar derived from biomass are the two primary sources for biological hydrogen production. Hydrogen production can be divided into a direct route, such as photolysis of water, and an indirect route, e.g. some organisms produce hydrogen from sugar [38]. In this process, hydrogen is produced from water using sunlight and specialized microorganisms, such as green algae and cyanobacteria. These microorganisms consume water and produce hydrogen as a byproduct of their natural metabolic processes, similar to the photosynthesis of plants to produce oxygen. Because the production of molecular hydrogen is rarely the purpose of natural biological system, the discussion of bio-hydrogen is limited in this work.

2.1.8 Photodissociation of water

Photoelectrochemical water splitting is a process analogous to photovoltaic devices aimed at electricity production. In this process, hydrogen is produced from water using sunlight and

specialized semiconductors called photoelectrochemical materials, such as TiO_2 [35]. In the photoelectrochemical system, the semiconductor uses light energy to directly dissociate water molecules into hydrogen and oxygen. Photobiological water splitting is in the very early stages of research, but offers long-term potential for sustainable hydrogen production with low environmental impact.

2.2 AQUEOUS PHASE REFORMING (APR)

We have discussed the different hydrogen production technologies, but our perspective for hydrogen production is that hydrogen should come from a renewable source, such as a biomass-related resource. One of the ideas is to produce hydrogen by a process called aqueous phase reforming (APR) of biomass-derived polyols.

2.2.1 Basis of the APR process

The idea of using aqueous phase reforming (APR) to produce hydrogen was first proposed by Dumesic and co-workers in 2002 [39]. The aqueous-phase reforming of polyols such as ethylene glycol and glycerol involves a process in which these compounds are catalytically converted into hydrogen and carbon dioxide in the aqueous phase with production of small amounts of hydrocarbons and other oxygenated species. Polyols are essentially oxygenated hydrocarbons with two or more neighboring hydroxyl groups. By elevating the system pressure over the feed bubble point pressure (the pressure at certain temperature when the first bubble of vapor formed during heating), essentially reactions occur in the aqueous phase, which makes it possible to keep

the reaction temperature low and reduce the level of carbon monoxide to a great extent via the water gas shift reaction. Two major reactions (reforming and the water gas shift) occur during the process:

$$C_nH_{2m}O_n \rightarrow n\,CO + m\,H_2 \quad (2.14)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (2.15)$$

Reforming of polyols generally denotes the overall reaction of oxygenated hydrocarbons and water to generate a hydrogen stream. In the water gas shift reaction, CO and H_2O are further converted to CO_2 and more hydrogen. Both reactions occur at the same relatively low temperature and can be conducted in the same reactor. Side reactions such as methanation reaction (2.16) and the Fischer-Tropsch reaction (2.17) may occur under aqueous phase reforming conditions [39-44].

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (2.16)$$

$$CO + H_2 \rightarrow C_nH_{2n+2} + C_mH_{2m} + C_kH_{2k+1}OH + H_2O \quad (2.17)$$

Hydrogen production using aqueous phase reforming of these oxygenated hydrocarbons has several advantages compared with steam reforming of natural gas [39, 45-46]:

- The process eliminates the need to vaporize both water and polyols, which lowers energy consumption for producing hydrogen.
- The process occurs at temperatures and pressures where the water-gas shift reaction is favorable, making it possible to generate hydrogen with low amounts of carbon monoxide in a single reactor.
- APR occurs at pressures (typically 30-80 bar) where the high pressure hydrogen rich effluent can be effectively purified and utilized for further purposes.

- APR can produce hydrogen from hard to evaporate polyols at relatively low temperatures in a single step process, in contrast to the multi-reactor steam reforming system required for producing hydrogen from hydrocarbons.
- The polyols of interest are from bio-sustainable sources and producing hydrogen from renewable resources helps to control greenhouse gas emissions.

Some of the disadvantages from aqueous phase reforming include:

- Reaction time from aqueous phase reforming (several minutes) is much longer than from steam reforming of methane (less than 1 second) [47].
- The high pressure environment and diluted feed solution add energy cost per unit of hydrogen production.
- Aqueous phase reforming uses noble metal (Pt) catalysts which add cost for hydrogen production.
- Aqueous phase reforming currently is only suitable for small scale hydrogen production.
- APR of sugars and sugar alcohols derived from food crops for hydrogen production uses arable lands and may lead to the eutrophication of water systems (an increase in chemical nutrients coming from fertilizers used for crop growth). This leads to excessive plant growth and decay in water and a further impact of lack of oxygen and severe reductions in water quality.

2.2.2 Thermodynamics

The aqueous phase reforming process can produce hydrogen from polyols with high boiling points (some above 300^{o}C) at relatively low temperatures (200^{o}C), which is much lower than the

temperature (above 700°C) required for steam reforming of methane. The wide temperature difference can be explained by the thermodynamics of the two reactions.

Davda and Dumesic compared reforming of alkanes with reforming of oxygenated hydrocarbons with C/O ratio of 1:1. They found that reforming these oxygenated hydrocarbons to produce CO_2 and hydrogen is thermodynamically favorable at significantly lower temperatures than those required for alkanes with similar numbers of carbon atoms. This offers a low-temperature route for the formation of hydrogen and CO_2 from polyols [46, 48].

2.2.3 Reaction pathways

A scheme of reaction pathways for aqueous phase reforming of ethylene glycol (EG), as shown in Figure 3, was proposed by Dumesic et al. [46, 48]. It is postulated that EG first dehydrogenates to give adsorbed intermediates, resulting in carbon-carbon (C-C) bond and carbon-oxygen (C-O) bond cleavage. The adsorbed species can be formed on the metal surface either by formation of metal–carbon or metal–oxygen bonds. It is reported that, on a metal catalyst such as platinum, the adsorbed species bonded to the surface by formation of Pt–C bonds are more stable than the species involving Pt–O bonds [39, 49], while the activation energy barriers for oxygen-hydrogen bonds (O-H) scission and carbon-hydrogen bonds (C-H) are similar [50]. Dumesic and co-workers predicted that the rate constant for the C-C bond cleavage is faster than for C-O bond cleavage on Pt surfaces at temperatures higher than 280°C [49].

In the scheme of reaction pathways for aqueous phase reforming of ethylene glycol [48], ethylene glycol first undergoes dehydrogenation steps to form adsorbed species on the metal surface; then three reaction pathways as indicated by (I), (II) and (III) are shown.

I. Ethylene glycol undergoes dehydrogenation to form an adsorbed species by formation of metal–carbon bonds. C–C bond cleavage then occurs to form intermediates which lead to formation of CO; CO reacts with water to form CO_2 and H_2 by the shift reaction [51, 52]. Methane and water could be formed by methanation or Fischer-Tropsch reactions [40-42]. Methanation steps decrease hydrogen selectivity.

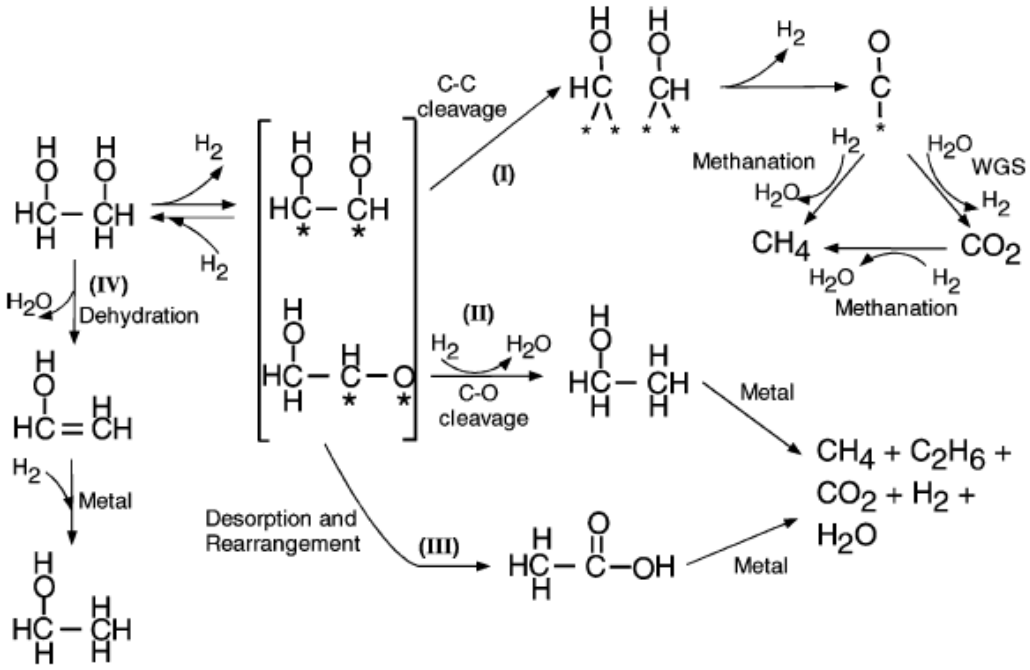


Figure 3. Possible reaction pathways for production of hydrogen from reactions of ethylene glycol with water [46, 48].

II. Ethylene glycol undergoes dehydrogenation to form the adsorbed species by formation of metal–oxygen bonds; then C-O bond scission occurs followed by hydrogenation to

form ethanol on the metal catalyst. The alcohol can further undergo C-C and C-O bond cleavage to methane, ethane, CO_2 and hydrogen. Ethanol can also dehydrate to ethylene (C_2H_4) and H_2O or decompose or crack to CH_4, CO and H_2. It can also reform with H_2O to CO_2 and H_2. This pathway results in a decrease of hydrogen selectivity.

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \quad (2.18)$$

$$C_2H_5OH \rightarrow CH_4 + CO + H_2 \quad (2.19)$$

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \quad (2.20)$$

III. Ethylene glycol undergoes dehydrogenation to form an adsorbed species by formation of metal–oxygen bonds. The species may rearrange to form an acid, which can then undergo surface reactions (adsorption, C–C cleavage, C–O cleavage) to form alkanes (CH_4 and C_2H_6), CO_2, H_2 and H_2O. Hydrogen selectivity is affected adversely in this way. Ethanol can be formed by dehydration of ethylene glycol to form an enol, following hydrogenation, as shown pathway IV.

2.2.4 APR Catalysts

The mechanism of hydrogen production by aqueous phase reforming involves the rupture and rearrangement of C-C and C-O bonds on the catalyst surface, leading to formation of intermediates which react with water to form hydrogen. An efficient catalyst should promote hydrogen formation (C–C scission [48] followed by the water-gas shift) and inhibition of alkane formation (C–O scission [48] followed by hydrogenation).

It has been reported that Group VIII metals generally have high activities for C-C bond breakage [53]. The relative rates of C-C bond cleavage, the water-gas shift reaction and

methanation for different metals are shown in Figure 4. Ru, Ni, Co, Fe and Rh showed high activity for C–C scission and for methanation. Cu exhibited high activity for the water-gas shift reaction, but no activity for C–C scission. Ir showed high C–C cleavage rates, but no activity for the shift reaction. It can be inferred that Pt and Pd should show suitable catalytic activity and selectivity for production of hydrogen by reforming of polyols, having reasonably high activities for C–C bond breaking and the shift reaction but low activity for methanation [48].

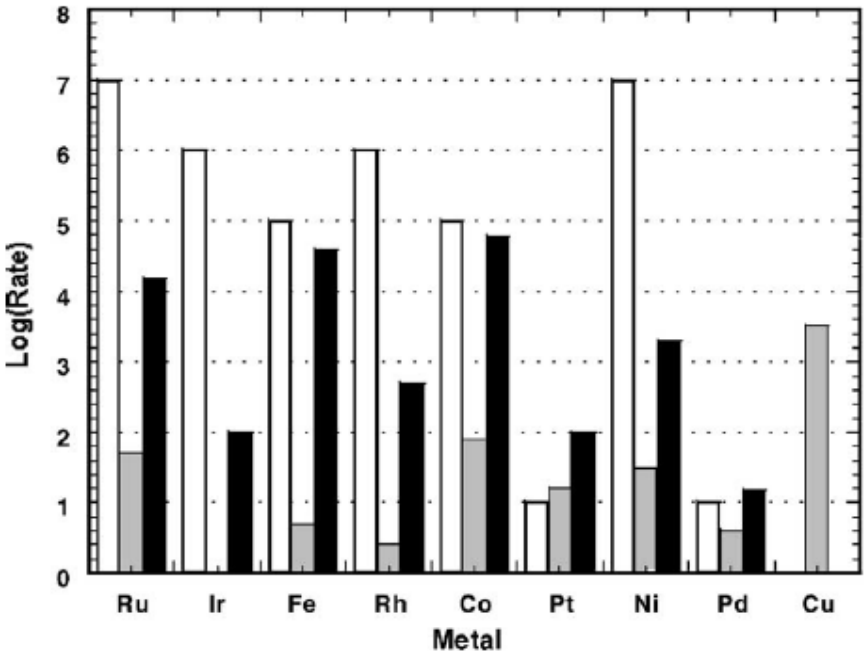


Figure 4. Relative rates of C–C bond breaking reaction (white), WGS reaction (gray), and methanation reaction [46, 48, 55-57].

Dumesic et al. [44, 48] have reported results of the aqueous-phase reforming of ethylene glycol over silica-supported group VIII metal catalysts at 483 K and 498 K in a fixed bed reactor. The rate of ethylene glycol reforming was found to decrease in the following order:

$$Pt \sim Ni > Ru > Rh \sim Pd > Ir$$

Silica supported Rh, Ru and Ni showed low selectivity for production of hydrogen and high selectivity for alkane production. While Pt, Ni and Ru exhibit relatively high activities for the reforming reaction, only Pt and Pd also show relatively high selectivity for the production of hydrogen. They suggested that Pt and Pd based catalysts as promising catalysts for further study. Huber et al. [45, 54] have reported using Sn promoted Raney-Ni catalyst to produce hydrogen. Due to their low cost and good catalytic activity, Ni-based catalysts are attractive despite their tendency to produce alkanes. They reported that the addition of Sn to Raney-Ni catalysts significantly decreased the rate of methane formation, while maintaining high rates of C–C cleavage necessary for production of hydrogen [54]. Shabaker et al. [43, 44] carried out the aqueous-phase reforming of ethylene glycol over various supported Pt catalysts to test the effect of the support on activity and selectivity for production of hydrogen. The supports included: TiO_2, Al_2O_3, SiO_2, ZrO_2, CeO_2, ZnO and carbon. Pt/Al_2O_3, and, to a lesser extent, Pt/ZrO_2 and Pt/TiO_2, were found to be active as well as selective catalysts for production of hydrogen by aqueous-phase reforming of ethylene glycol.

Dumesic and coworkers have started a broad research on aqueous phase reforming for hydrogen production. Guided by his inspiring idea, my work starts on similar substances and explores a wide selection of renewable polyols, such as glycerol, mannitol, sorbitol, glucose, sucrose, table sugar and corn syrup. The intent of my research is to extend the aqueous phase reforming technology on more polyols, especially those who are widely available and

economically competitive. Works need to be done to realize the goal, such as finding a proper catalyst and optimal operation conditions, investigating the structure of the polyols and kinetics to help understand the mechanism of APR.

3.0 EXPERIMENTAL METHODS

3.1 CATALYST PREPARATION

Alumina-supported platinum catalysts were prepared by incipient wetness impregnation methods. The precursor for deposition of Pt on γ-alumina was tetraammineplatinum nitrate ($Pt(NH_2)_4(NO_3)_2$). An aqueous solution of the Pt salt was added dropwise to the Al_2O_3 while stirring. The take-up of the solution is governed by the porosity of the support; the volume of the solution is empirically determined to correspond to that beyond which the catalyst begins to look wet. Different supports have different water absorption capacity. The amounts of water needed for the impregnation were tested and the ratios between water solution and support are listed in the appendix C. After absorption of the solution into the pore system of the support, a drying stage is used to remove water, so that the impregnated component remains within the support pore system and does not migrate to the exterior surface of the support. Catalysts were dried in an oven at 100^{o}C overnight. Catalysts were calcined in air after drying, converting the soluble salt to insoluble oxide. The calcinations lasted for 2 hours at 260˚C. Platinum catalysts on TiO_2, ZrO_2, SiO_2 and MgO were also prepared following the same procedure. The starting chemical materials used for preparation of catalysts are listed in Table 2.

Table 2. Starting chemicals for catalyst preparation

Chemicals	Formula	Purity	Source
Pt Precursor	$Pt(NH_2)_4(NO_3)_2$	99.9%	Strem Chemical
Support	γ-Al_2O_3	99.99%	Aldrich Chemical
	TiO_2	99.9%	Degussa
	SiO_2	99.95%	Aldrich Chemical
	MgO	99.5%	Aldrich Chemical
	$Zr(OH)_4$	99.9%	MEI

3.2 EXPERIMENAL SYSTEMS

Aqueous phase reforming of ethylene glycol for hydrogen production was first carried out in a microautoclave reactor system. A continuous reactor was then set up to study kinetics of the reactions. In these studies, the experimental conditions, such as catalyst, catalyst support, reaction temperature, reaction pressure, and feedstock were varied and their effect on the reactant conversions and product selectivities were monitored and studied. Hydrogen production from glycerol, sorbitol, mannitol, glucose and sucrose were also investigated.

3.2.1 Batch system

Aqueous-phase reforming of ethylene glycol was carried out in a batch system using a horizontal shaking 40 ml microautoclave. After 0.5 g catalyst was loaded, the reactor was purged with helium and pressurized to 300 psi at room temperature to test for leaks. The reactor was then purged four times with helium to remove air. It was then purged with hydrogen and pressurized to 400 psi at 250^{o}C for 30 minutes to reduce the catalyst. After reduction, the system was cooled to room temperature. The system was purged with helium four times to remove hydrogen and then the pressure was released. Helium was purged again after a 15ml liquid solution of 10 wt% ethylene glycol in deionized water was introduced into the reactor with a syringe pump; the system pressure was then kept at 450 psi. The reactor was then immersed into a fluidized sand bath and heated to the final reaction temperature. The reactor was shaken horizontally at 180 cycles per minute. The reaction was terminated by removal from the sand bath and immediately cooled with running cold water. Before opening the reactor to collect the liquid product, the gas products were sampled and analyzed by GC (HP6890). The liquid product was analyzed by another GC (HP5890).

3.2.2 Continuous system

The reaction was carried out in a computer controlled fixed-bed reactor housed in a furnace. The catalyst was loaded in the middle of a 3/8 inch od and 1/4 inch id stainless-steel tubular reactor as a packed bed about 10 mm long. The temperature of the reactor was monitored using a Chromomega-Alomega K-type thermocouple inserted into the middle of the catalyst bed in the reactor. There are two gas inlets in the system, one for hydrogen and one for nitrogen. Prior to

reaction, the fresh catalyst was reduced in flowing hydrogen at a rate of 50 ml/min. The catalyst was heated, using a linear temperature program ramping from room temperature to the final reduction temperature at a rate of 1^{o}C/min, holding at that temperature for 2 hours and then cooling to room temperature, all in flowing hydrogen purified by flowing through a desiccator bed of activated molecular sieves at room temperature. The flow rate of hydrogen (or nitrogen) was controlled using mass flow meters (Brooks 5850E). Calibrations of flow rate of hydrogen and nitrogen were carried out regularly. After reduction, the system was switched to nitrogen as the carrier gas and pressurized to the desired pressure. Nitrogen was purified by flowing through a desiccator bed of activated molecular sieves at room temperature. A liquid solution of polyols in deionized water with a desired concentration was introduced into the reactor in an upflow configuration with a syringe pump (ISCO 500D). The overall pressure of the system was regulated by a back-pressure regulator (TESCOM regulator, model No. 26-1766-24-154). The steam saturation pressure as a function of temperature is shown in Figure 5. The system pressures lie in the range from 300 psi to 1000 psi. The relatively high pressure required at high temperatures is a challenge to reactor design; there is a strong benefit from low temperature aqueous phase reforming.

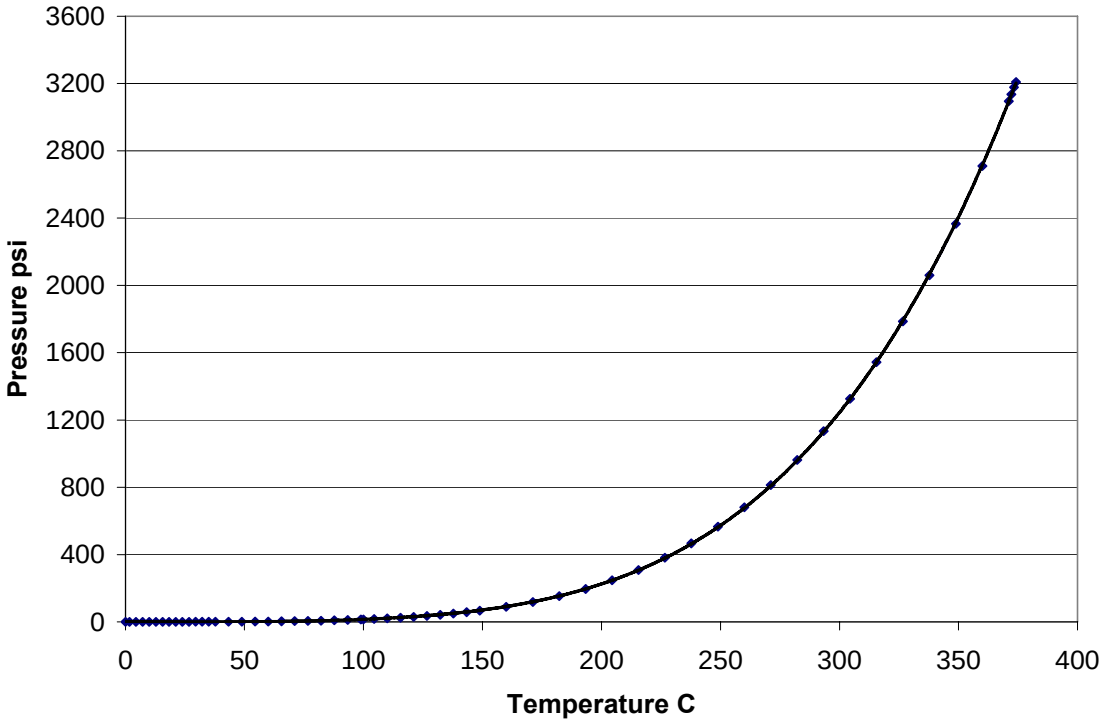


Figure 5. Steam saturation pressure at different temperatures

For the Pt catalyst used in the aqueous phase reforming of polyols, there was an induction period when no hydrogen formation was observed. After the induction period was over, the system was operated for more than six hours to reach a steady state at the desired temperature, as shown from the hydrogen production rate. The feed from the pump was set at the desired flowrate. The effluent from the reactor was cooled to room temperature in the liquid-gas separator. The fluid was then contacted with nitrogen, which bubbled through the effluent to sweep out the gaseous products, while the liquid effluent collected in the separator. The liquid product was drained periodically for analysis using GC and GCMS. The gas effluents passed

through the back pressure regulator and were analyzed by online GC. After taking a liquid sample, the system was held at that temperature and pressure for about 3 hours until hydrogen formation returned to the steady state again before changing the operating temperature and pressure. A diagram of the continuous system is shown in Figure 6.

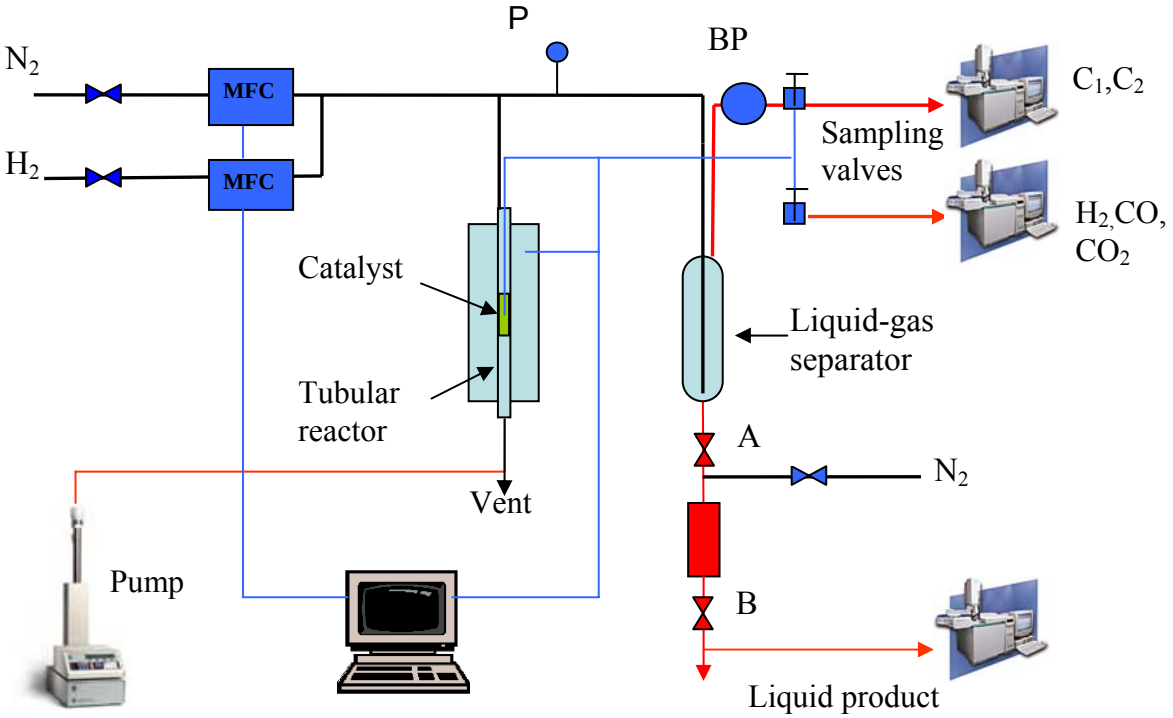


Figure 6. Sketch of the continuous system for aqueous-phase reforming of polyols

3.3 PRODUCT SAMPLING AND ANALYSIS

To prevent a pressure drop during samples collection and temperature fluctuation caused by pressure drop after the collection, nitrogen gas was introduced between the separator and the liquid trap as shown in Figure 6. To take a liquid sample, valve A was closed and liquid removed; then valve B was closed and nitrogen gas was introduced into the system so that there was no pressure drop when valve A was opened again.

Liquid products were analyzed by a gas chromatograph (HP 5890 GC) equipped with a flame-ionization detector (FID) through an Ecwax capillary column and a gas chromatograph mass spectrometry (GC-MS) equipped with a FID detector through a HP-5 capillary column. A stream of effluent gas went through two automatic sampling valves controlled by a computer and analyzed by an online GC equipped with both a flame-ionization detector (FID) and a thermal conductivity detector (TCD). Hydrogen, carbon monoxide and carbon dioxide were separated via a Carbosieve column connected to the TCD detector, while methane, ethane, propane and other hydrocarbons were separated via a Porapak Q column connected to the FID detector.

Calibrations of both gas chromatographs were carried out regularly. The carbon monoxide gas calibrations were carried out using a standard gas mixture of CO and helium from Linde Gas (500 ppm CO and He as the balance gas). Hydrogen, methane, ethane and other hydrocarbons calibrations were carried out using a standard gas mixture from Praxair (5% H_2, 1% CH_4, 1% C_2H_6 and Ar as the balance gas).

3.4 REACTANTS

Our studies were concerned with the production of hydrogen from polyols, which are oxygenated hydrocarbons with two or more neighboring hydroxyl groups (e.g. ethylene glycol, glycerol, sorbitol, mannitol, glucose and sucrose). They usually have a carbon to oxygen ratio of 1:1, with each carbon bonded to a hydroxyl group. We also studied the aqueous phase reforming of polyethylene glycol. Sugars (sucrose, glucose and corn syrup) and sugar alcohols (sorbitol and mannitol) were also investigated as possible sources for hydrogen.

3.4.1 Ethylene glycol

Ethylene glycol ($HOCH_2CH_2OH$) is the simplest polyol; it has two hydroxyl groups, each bonded to a carbon atom. It is widely used as an automotive antifreeze. In its pure form, it is an odorless, colorless, syrupy liquid with a sweet taste and a boiling point of 197^{o}C. At present, ethylene glycol is made from ethylene, derived from petroleum, via the intermediate ethylene oxide which reacts with water to produce ethylene glycol (Figure 7). It can also be produced from synthesis gas via a process which involves the oxidative carbonylation of methanol to dimethyl oxalate, followed by hydrogenolysis to ethylene glycol and to methanol, which is recycled (Figure 8). Ethylene glycol can also be derived from renewable sources, such as glycerol or sorbitol, through hydrogenolysis processes [59-60].

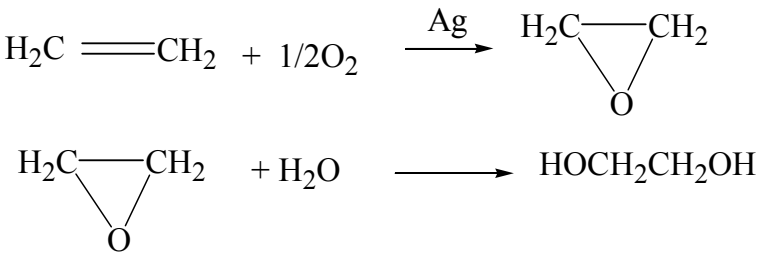


Figure 7. Ethylene glycol synthesis from ethylene

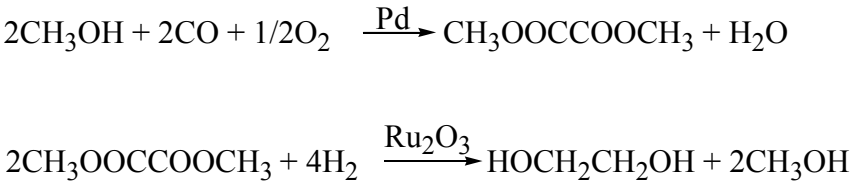


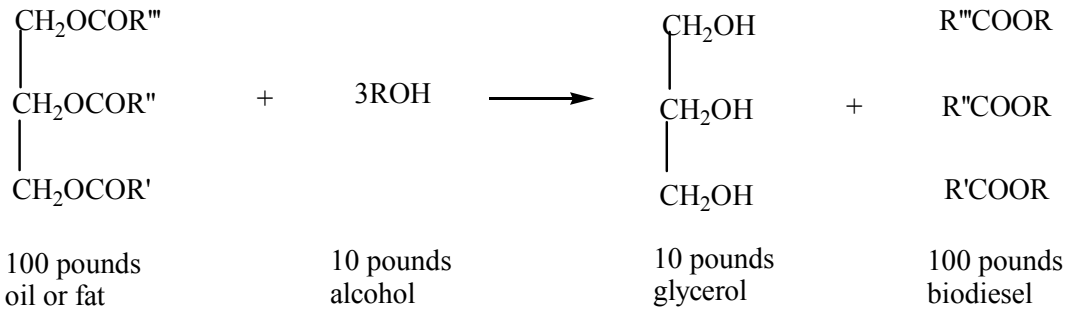
Figure 8. Ethylene glycol synthesis from methanol

3.4.2 Glycerol

Glycerol is a colorless, odorless, hygroscopic, and sweet tasting viscous liquid, with a boiling point of 290°C. It has three hydrophilic alcoholic hydroxyl groups that are responsible for its solubility in water. Glycerol is present as the backbone in the form of its esters (glycerides) in all animal and vegetable fats and oils. Glycerol was mainly manufactured industrially from

epichlorohydrin (1-chloro-2,3-epoxypropane) though this process is no longer economical; it is now obtained commercially as a byproduct in the saponification (hydrolysis of an ester under basic conditions to form an alcohol and the salt of a carboxylic acid) or transesterification (exchange the alkoxy group of an ester compound by another alcohol) of fats and oil to make soap or biodiesel. Biodiesel (fatty acid alkyl esters) is a clean burning diesel replacement fuel made from natural, renewable sources such as new and used vegetable oils and animal fats in a process called transesterification, as shown in Figure 9. It is a biodegradable fuel; its use reduces serious air pollutants.

The biodiesel industry has grown rapidly in the past five years. According to the National Biodiesel Board, U.S. biodiesel demand in 2006 was 225 million gallons [5]. There are presently (June 2007) 148 companies in the development of biodiesel manufacturing plants marketing biodiesel with an annual production capacity of 1.38 billion gallons per year [58]. Ninety-three companies have reported that plants are currently under construction and are scheduled to be completed within the next 18 months. An additional five plants are expanding their existing operations. Their combined capacity would result in another 1.85 billion gallons per year of biodiesel production [58]. About one pound of glycerol is produced for every ten pounds of biodiesel; or three quarter of a pound of glycerol is produced for every gallon of biodiesel. Biodiesel production is predicted to yield an additional 1 billion lb of glycerol over the next two years [9]. Finding new outlets for the overcapacity of glycerol has attracted great interest.



* R', R'' and R''' indicate alkyl chains from C_{12} to C_{18}

Figure 9. Transesterification process to make biodiesel and glycerol

3.4.3 Polyethylene glycol (PEG)

PEG is a water-soluble organic polymer that is used extensively in the cosmetic and toiletry industry for the preparation of emulsifying agents, plasticizers and textile lubricants. We used PEG-200 (from Aldrich Chemical) in our experiments; it is a mixture of polymerization products of ethylene glycol，including diethylene glycol, triethylene glycol, tetraethylene glycol and so on, with an average molecular weight of 200. Its formula may be written as $HO(CH_2CH_2O)_nH$, where n is between 2 to 6. Figure 10 shows the GC-MS image of PEG 200 in water solution.

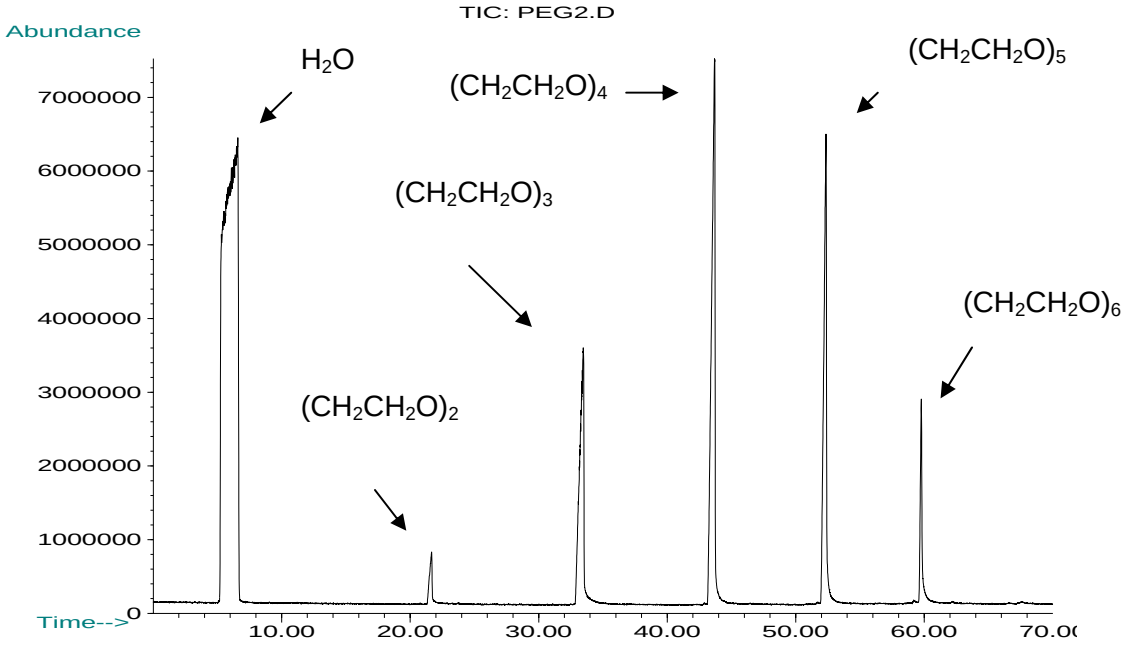


Figure 10. GCMS of 10 wt% PEG-200 in water solution

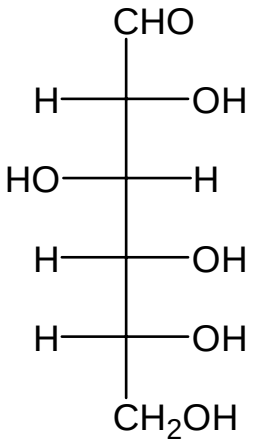
3.4.4 Sugars and sugar alcohols

Glucose is a monosaccharide and one of the most important carbohydrates in plants and in animals. It is used as a source of energy and as a metabolic intermediate. Glucose ($C_6H_{12}O_6$), an aldohexose, contains six carbon atoms. The glucose molecule can exist in an open-chain (acyclic) and ring (cyclic) form. In the cyclic form, an intramolecular reaction between the aldehyde carbon atom and the C-5 hydroxyl group forms an intramolecular hemiacetal. In this ring, each carbon is linked to a hydroxyl side group with the exception of the fifth atom, which

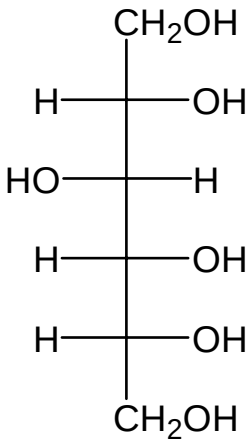
links to a sixth carbon atom outside the ring, forming a CH_2OH group. In water solution both forms are in equilibrium and at pH of 7 the cyclic one is predominant.

Sucrose is a disaccharide with the molecular formula of $C_{12}H_{22}O_{11}$. This most widely occurring disaccharide is found in all photosynthetic plants and is obtained commercially from sugar cane and sugar beets. Hydrolysis of one mole of sucrose yields one mole of glucose and one mole of fructose. Sorbitol is a sugar alcohol the body metabolizes slowly. It is obtained by reduction of glucose, in which the aldehyde group is reduced to an additional hydroxyl group. Sorbitol is widely used in food and medicine. It is a sugar substitute often used in diet foods. Sorbitol is also referred to as a nutritive sweetener because it provides fewer calories or energy to the diet, compared with sugar and starch, while retaining 60% of the sweetness. Mannitol is an isomer of sorbitol. Sorbitol and mannitol both have the same molecular formula but differ in the configuration of the hydroxyl groups on the carbon chain. Figure 11 shows the chain and ring structures of glucose, sorbitol, mannitol and sucrose.

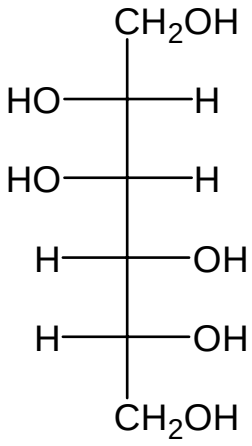
Glycerol, mannitol, sorbitol, glucose and sucrose are renewable polyols. Hydrogen obtained from them by the aqueous phase reforming and used to power fuel cells will have low net greenhouse gas emissions and will help to reduce pollutions



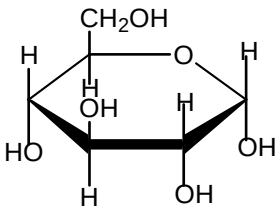
Glucose



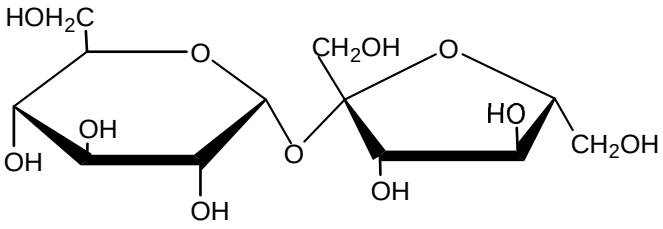
Sorbitol



mannitol



D-glucose



Sucrose

Figure 11. Structures of glucose, sorbitol, mannitol and sucrose

4.0 THERMODYNAMIC CALCULATIONS OF AQUEOUS PHASE REFORMING OF POLYOLS

Studies have been conducted on thermodynamic calculations of hydrogen production through different technologies [61-65]. Cunping [61-62] reported thermodynamic analysis of hydrogen generation from natural gas by steam reforming, autothermal reforming and pyrolysis. Andrew has studied steam reforming of other alkanes to produce hydrogen [63]. Ekaterini [64] published a study on the thermodynamic calculation of steam reforming of bio-oil fractions. Sushil [65] reported a thermodynamic analysis of steam reforming of glycerol. Here we present a thermodynamic analysis of aqueous phase reforming of glycerol and other polyols. The aim of the study is to analyze the production of hydrogen by low temperature reforming of polyols and compare it with other processes such as steam reforming. It also provides an explanation for how and why low temperature reforming of these compounds can take place leading to the formation of hydrogen with very low amounts of carbon monoxide.

4.1 METHODOLOGY

In chemical reactions, equilibrium is the state in which the chemical activities or concentrations of the reactants and products have no net change over time. In thermodynamics, the Gibbs free energy serves as a thermodynamic potential which measures the process-initiating work

obtainable from a thermodynamic system. Gibbs energy is defined as a combination property of enthalpy and entropy.

$$G = H - TS \tag{4.1}$$

or equivalently,

$$G = \sum \mu_i N_i \tag{4.2}$$

where, μ_i is the chemical potential of the i^{th} chemical component of the system and N_i is the number of particles (or number of moles) of the i^{th} chemical component.

Gibbs energy is minimized when a system reaches equilibrium at constant pressure. Therefore, by minimizing the Gibbs free energy, the equilibrium conditions can be obtained thermodynamically. The objective is to find the set of N_i values that minimize the value of G. This can be solved in two ways: stoichiometric thermodynamic method and nonstoichiometric thermodynamic method. In the stoichiometric thermodynamic approach, the system is described by a set of independent stoichiometric reactions, which are typically chosen from a series of possible reactions. In the nonstoichiometric approach, the equilibrium condition is obtained by the minimization of the Gibbs free energy for a given set of species. Both the stoichiometric and nonstoichiometric methods are typically used to describe the equilibrium conditions of a closed system. However, obtaining the equilibrium conditions of the system from the nonstoichiometric approach is more general than from the stoichiometric approach, because the selection of the series of independent reactions and an estimation of the initial equilibrium conditions are not necessary for the nonstoichiometric approach, and there is no divergence during the computation in the nonstoichiometric approach. In this work, we use the nonstoichiometric approach to calculate the equilibrium conditions for hydrogen production from reforming of polyols as well as from alkanes. The possible products from reforming include hydrogen (H_2), carbon dioxide

(CO_2), methane (CH_4), ethane (C_2H_6), propane (C_3H_8), carbon monoxide (CO), water and unreacted reactants. Those are the major products in the reforming reactions carried out in our laboratory. Although carbon deposition onto catalysts may occur in the experiments, we did not consider it in our thermodynamic calculations. Alkene formation is also assumed negligible in the calculation.

ASPENPLUS 11.1 software is used for these thermodynamic calculations. This requires specification of the system, such as the reactor and the separator. In most cases, RGibbs reactor is selected for the calculations. Other reactors, such as RStoic reactor and REquil reactor are also used for calculations. A flash separator is used to obtain some physical properties, such as solubility. Physical properties were calculated using Peng–Robinson, NRTL and UNIFAC method.

4.2 THERMODYNAMIC ANALYSIS

Hydrogen is commercially produced by steam reforming of natural gas, including methane and other light alkanes. These are highly endothermic reactions, with a reaction temperature range from 700^{o}C to 1000^{o}C. The water gas shift reaction is introduced as an extra step to convert carbon monoxide to carbon dioxide and produce more hydrogen. The stoichiometric reactions are shown below.

$$C_nH_{2m} + nH_2O = nCO + (m+n)H_2 \quad (4.3)$$

$$H_2O + CO = H_2 + CO_2 \quad (2.2)$$

$$\text{Total reaction } C_nH_{2m} + 2nH_2O = nCO_2 + (m+n)H_2 \quad (4.4)$$

The reactions for aqueous phase reforming of polyols with a carbon to oxygen ratio of 1:1 to produce hydrogen are shown by the following equations. Polyols may undergo the reforming reaction to carbon monoxide and hydrogen; the water gas shift reaction may occur to convert carbon monoxide to carbon dioxide.

$$C_nH_{2m}O_n = nCO + mH_2 \quad (4.5)$$

$$H_2O + CO = H_2 + CO_2 \quad (2.2)$$

$$\text{Total reaction } C_nH_{2m}O_n + nH_2O = nCO_2 + (m+n)H_2 \quad (4.6)$$

The temperature required to convert a polyol to hydrogen in aqueous phase reforming is around 200^{o}C. It is possible that the intermolecular actions between the hydroxyl groups weaken the C-C bond in the polyol so it is easier to break than the C-C bond in an alkane with the same number of carbon atoms.

The reforming reaction conditions, such as temperature, are related to the thermodynamics of the reactions themselves. The Gibbs free energy associated with a reaction is a thermodynamic potential which measures the spontaneity of the reactions, as follows.

$\Delta G < 0$	The reaction is spontaneous
$\Delta G = 0$	The reaction is at equilibrium
$\Delta G > 0$	The reaction is nonspontaneous

Let us take the reactions of steam reforming of methane, the water gas shift reaction, and the aqueous phase reforming of glycerol as examples. The reactions are shown below.

$$CH_4 + H_2O = CO + 3H_2 \quad (2.1)$$

$$H_2O + CO = CO_2 + H_2 \quad (2.2)$$

$$C_3H_8O_3 + 3H_2O = 3CO_2 + 7H_2 \quad (4.7)$$

Figure 12 shows the Gibbs free energy versus temperature for the reactions including: the steam reforming of methane, the water gas shift reaction, the methanation reaction and the aqueous phase reforming of glycerol. The reaction for steam reforming of methane, as shown by the top curve (▲), is thermodynamically favorable ($\Delta G < 0$, spontaneous reaction) only above a temperature of 630^{o}C; however, the temperature required for the aqueous phase reforming of glycerol, as shown by the dashed line curve, is thermodynamically favorable above 150^{o}C, which is significantly lower than the temperature for steam reforming of methane. Moreover, the water gas shift reaction, as shown by the curve (■), is also thermodynamically favorable at the same low temperature. Therefore, unlike steam reforming of methane, which requires extra steps of water gas shift reactions to significantly remove carbon monoxide during the production of hydrogen, aqueous phase reforming can easily incorporate the water gas shift reaction to convert carbon monoxide to carbon dioxide and more hydrogen in a single step reactor, saving energy and cost.

Dumesic compared steam reforming of alkanes (methane to hexane) with steam reforming of oxygenated hydrocarbons (methanol to sorbitol); in our calculations we chose conditions to fit in the liquid phase reforming (operation pressures above the feed bubble point pressures); therefore our thermodynamic calculations resemble the experiment results.

It is indicated that it is possible to produce hydrogen from glycerol in water solution at a temperature around 200^{o}C. Similar calculations also show that it is possible to produce hydrogen from other polyols, such as erythritol, sorbitol and mannitol, which are oxygenated hydrocarbons with limited volatility. It is difficult to convert them to hydrogen using steam reforming because of their high boiling points. By reforming these molecules in the liquid

phase, the need to vaporize the polyols is eliminated. The energy needed to supply the heat of vaporization of the reactants is also eliminated.

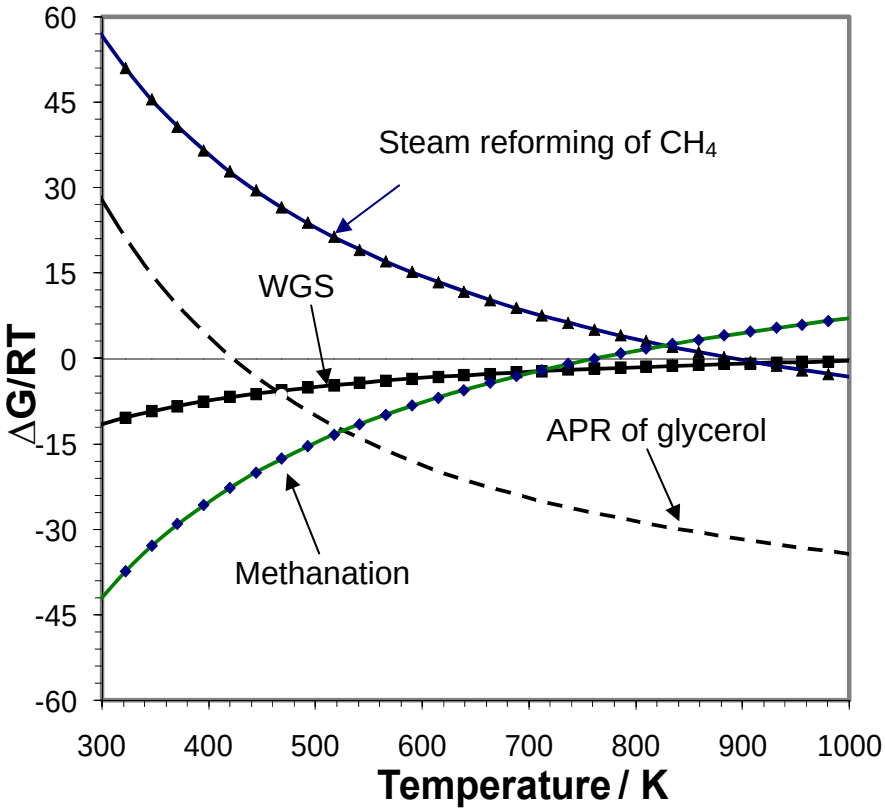


Figure 12. Gibbs free energy for the steam reforming of methane, the water gas shift reaction, the methanation reaction and the aqueous phase reforming reaction of glycerol as a function of temperature

Aqueous phase reforming provides an alternate route to produce hydrogen from those low-volatile polyols at dramatically low temperatures, around 200°C. In order to do this, the

system must operate at elevated pressure, above the bubble point pressure (the pressure at which the first bubble is formed at certain temperature) of the feed at a particular temperature to maintain the aqueous phase. The equilibrium conversion for aqueous reforming of ethylene glycol is shown in Figure 13, where the percent of ethylene glycol converted is plotted versus temperature at a pressure of 450 psi. The change in conversion of ethylene glycol is dramatic, rising from 4.6% converted at 166˚C to 99.8% at 169˚C. The almost complete conversion of ethylene glycol is due to the removal of the products (H_2 and CO_2) from the liquid phase in which the reaction is taking place while ethylene glycol, which has a low vapor pressure (27 psi at 220˚C), remains almost completely in the liquid phase. The results also show that the carbon monoxide concentration in the system can be kept below 500 ppm, which indicates that low temperature reforming favors the water gas shift reaction so that carbon monoxide is converted almost completely to carbon dioxide.

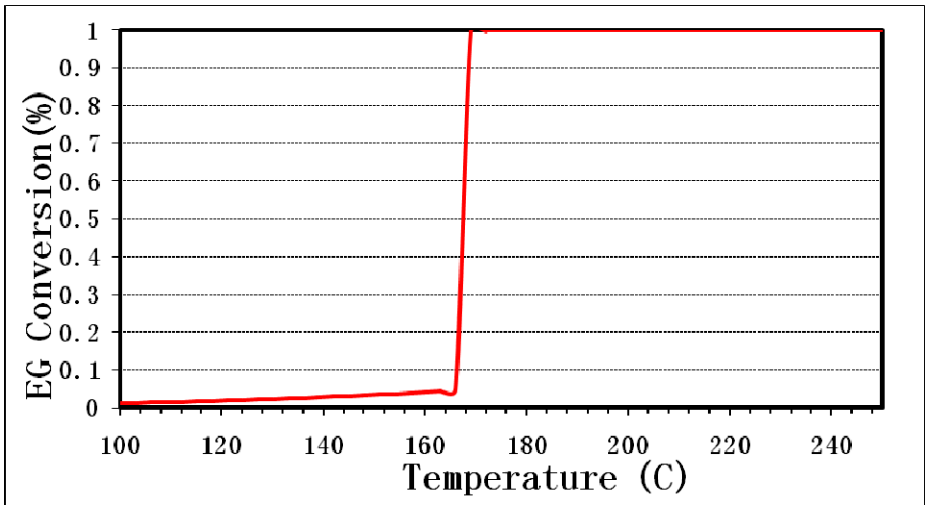


Figure 13. Equilibrium conversion of ethylene glycol by aqueous phase reforming at 450psi

It is speculated that the number and positions of hydroxyl groups in the carbon chain of oxygenated hydrocarbons might affect hydrogen production. We compared ethane with ethanol and ethylene glycol. Each compound has two carbon atoms but the number and position of any hydroxyl groups vary; we also compared propylene with propanol, 1,2-propanediol and glycerol. Each molecule has three carbon atoms but the number and position of any hydroxyl groups are different. Gibbs reactor was used to calculate the equilibrium conditions. By minimizing the Gibbs free energy of the reaction system, the equilibrium temperature, composition and reactant conversion could be calculated. Steam reforming is used for alkanes, while alcohols and polyols undergo aqueous phase reforming. Tables 3 and 4 show the temperature for three levels of conversion of reactants with no or varying numbers of hydroxyl groups.

Table 3. Equilibrium temperature at three conversion levels for ethylene, ethanol and ethylene glycol

	Temperature @ 50% conversion	Temperature@ 75% conversion	Temperature@ > 99.9% conversion
Ethane CH_3CH_3	456 ^oC	520 ^oC	704 ^oC
Ethanol CH_3CH_2OH	220^oC	245^oC	300^oC
Ethylene glycol $HOCH_2CH_2OH$	170^oC	176^oC	180^oC

*Gibbs reactor was used to simulate the steam reforming of ethane, aqueous phase reforming of ethanol and of ethylene glycol using ASPENPLUS; pressure for steam reforming of ethane was kept at 100 psi and for aqueous phase reforming of ethanol and of ethylene glycol was kept at 450 psi

There is a large difference between the temperature required for the conversion of alkanes and for the conversion of alcohols, as well as polyols. Molecules with one or more hydroxyl groups have a lower temperature for reforming at desired conversions than molecules with no hydroxyl groups or a smaller number of hydroxyl groups; e.g., for the two carbon chain series of alkanes and polyols, the temperature required for steam reforming of ethane with a high conversion (>99.9%) is 704^{o}C, which is 524^{o}C higher than the temperature required for aqueous phase reforming of ethylene glycol and 404^{o}C higher than the temperature required for reforming of ethanol at the same conversion. Aqueous phase reforming of ethanol at nearly 100% conversion is at 300^{o}C, which is 120^{o}C higher than required for aqueous phase reforming of ethylene glycol. The trend also applies at lower conversions (50% and 75%). The equilibrium temperatures to produce hydrogen from the alkane, alcohol and polyol at a desired conversion decreases as the number of hydroxyl groups increases.

For the three carbon chain series of alkane, alcohol and polyols, results in Table 4 show that the temperature required for steam reforming of propane at nearly 100% conversion is 710^{o}C, which is over 500^{o}C higher than the temperature required for reforming of glycerol, 380^{o}C higher than the temperature of reforming 1-propanol, and 480^{o}C higher than the temperature for 1,2-propanediol. The same trend occurs at lower conversions (50% and 75%). Not only does addition of hydroxyl groups to neighboring carbon atoms help lower the temperature for the reforming of polyols for desired conversions, but also as more hydroxyl groups are bonded to carbon atoms in the chain, the reactants can be reformed to hydrogen and carbon dioxide at even lower temperature.

Table 4. Equilibrium temperature conditions at three conversion levels for propane, 1-propanol, 1,2-propanediol and glycerol

	Temperature @ 50% conversion	Temperature @ 75% conversion	Temperature @ > 99.9% conversion
Propane $CH_3CH_2CH_3$	400°C	610°C	710°C
1-Propanol $CH_3CH_2CH_2OH$	240°C	265°C	330°C
1,2-Propanediol $CH_3CHOHCH_2OH$	212°C	218°C	230°C
Glycerol $CH_2OHCHOHCH_2OH$	144°C	150°C	160°C

*Gibbs reactor was used to simulate the steam reforming of propane, aqueous phase reforming of 1-propanol, 1,2-propanediol and glycerol using ASPENPLUS; pressure for steam reforming of propane was kept at 100 psi and for aqueous phase reforming of 1-propanol, 1,2-propanediol or glycerol was kept at 450 psi

These trends could be explained by the bond energy required to break the C-C bond. The mechanism of H_2 production from reforming of polyols, alcohols or alkanes with at least two carbon atoms involves the rupture and rearrangement of the C-C bonds and other bonds on the catalyst surface leading to the formation of intermediates which react with water to form H_2 and CO or CO_2. In order to compare the C-C bond energy for alkanes, alcohols and polyols, computations were performed using density functional theory (DFT) to calculate the C-C bond energies and the C-C bond distances. Density functional theory is a quantum mechanical method used to investigate the electronic structure of particular molecules. Students from Dr. Karl Johnson's group at the Department of Chemical and Petroleum Engineering provided assistance

in carrying out the calculations. The details of the calculations are described elsewhere [66-68]. The simulation results are shown in Tables 5 and 6.

Table 5. Comparison of bond energies and bond distances between ethane and ethylene glycol

	C-C bond energy kJ/mol	C-C Distance(Å)
Ethane CH_3-CH_3	390	1.53
Ethylene glycol $HOCH_2$-CH_2OH	337	1.52

The calculations show that addition of hydroxyl groups to the carbon atoms in polyols significantly lowers the C-C bond energy, e.g., the C-C bond energy in ethylene glycol is 337 kJ/mol, which is 53 kJ/mol less than the C-C bond energy in ethane; the C-C bond energy in glycerol is 332 kJ/mol, which is 43 kJ/mol less than the C-C bond energy in propane. However, addition of hydroxyl groups has a very small impact on the C-C bond distance.

The distance between the hydroxyl groups seems to influence the C-C bond energy. As shown in Table 6, the closer the hydroxyl groups, the weaker the C-C bond energy, e.g., in 1,2-propanediol, the C-C bond energy between the first and second carbon atoms is 342 kJ/mol, which is 22 kJ/mol less than the C-C bond energy between the first and second carbon atoms in 1,3-propanediol.

Table 6. Comparison of bond energies and bond distances for propane, 1-propanol, glycerol, 1,2-propanediol and 1,3-propanediol

	C_1-C_2 bond energy kJ/mol	C_2-C_3 bond energy kJ/mol	C1-C2 Distance(Å)	C2-C3 Distance(Å)
Propane $^1CH_3$-$^2CH_2$-$^3CH_3$	375	375	1.53	1.53
1-Propanol $HOCH_2$-CH_2-CH_3	353	384	1.52	1.53
1,2-Propandiol $HOCH_2$-CHOH-CH_3	342	370	1.53	1.53
1,3-Propandiol $HOCH_2$-CH_2-CH_2OH	364	364	1.52	1.52
Glycerol $HOCH_2$-CHOH-CH_2OH	332	332	1.53	1.53

4.3 EQUILIBRIUM COMPOSITION OF AQUEOUS PHASE REFORMING OF GLYCEROL

Steam reforming of methane is a strongly endothermic reaction. Methane reacts with high temperature steam (700~1000^oC) under 3-25 bar pressure in the presence of a catalyst to produce a mixture of hydrogen, carbon monoxide and carbon dioxide. Because steam reforming occurs at high temperatures, the water gas shift reaction is not favorable inside the reactor. The gas mixture then undergoes extra steps of water gas shift reactions in separate reactors to convert CO to CO_2, which makes the whole process complicated and energy intensive. Aqueous phase

reforming of polyols occurs at much milder conditions, at around 200^{o}C, much lower than the conventional steam reforming temperature. The low temperature also favors the water gas shift reaction, making it possible to incorporate the water gas shift reaction with reforming in the same reactor to generate H_2 with low amounts of CO.

The thermodynamic analysis was performed over the following ranges-- 40 to 1326 psi, 130 to 300^{o}C and 0.01 to 0.1 ratios of glycerol to water. The system pressures were kept at the water vapor pressure at certain temperatures to perform the reaction in aqueous phase. Equilibrium concentrations were calculated using ASPENPLUS software by direct minimization of the Gibbs free energy of a two phase mixture of water and glycerol undergoing reactions that leads to production of H_2, CO, CO_2, CH_4, C_2H_6 and C_3H_8. The equilibrium gas phase contained negligible amounts of ethane, propane and glycerol. The concentrations of other products are shown in Figure 14 on a water-free basis.

Results show that under aqueous phase reforming conditions, CO accounts for less than 500ppm (0.0005) below 250^{o}C; the rest is H_2 rich gas, including mostly H_2 and CO_2 with a small amount of CH_4. Examination of Figure 14 reveals that higher temperatures favor the production of hydrogen which is desirable but also favor the production of CO, which is undesirable, suggesting that operation from 200 to 250^{o}C at a pressure high enough to maintain a liquid phase would be good operating conditions for experimental investigations

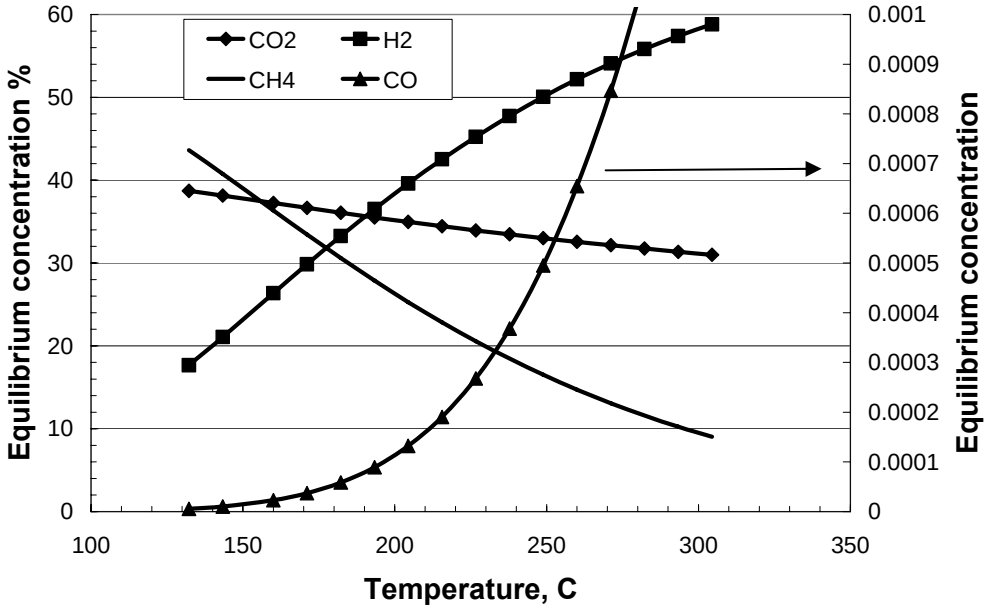


Figure 14. Equilibrium concentrations (water free base) of CO_2, H_2, CH_4 and CO in aqueous phase reforming of 10 wt% glycerol in water solution

4.4 EQUILIBRIUM COMPOSITION OF STEAM REFORMING OF GLYCEROL

The production of hydrogen from steam reforming of glycerol was also studied using thermodynamic calculation. Glycerol and water steam are introduced in the ambient pressure Gibbs reactor. Similar to the aqueous phase reforming, the major product in the gas steam include: hydrogen, carbon dioxide, carbon monoxide and methane. Glycerol is all converted and ethane and propane are negligible. Figure 15 shows the equilibrium concentrations (water free

base) of CO_2, H_2, CH_4 and CO in steam reforming of glycerol. Hydrogen concentration increases with temperature and maximizes at 550°C and then decreases slowly with temperature; carbon dioxide concentration decreases with rising temperature more slowly compared with methane. Carbon monoxide concentration is less than 100 ppm when temperature is below 150°C; it then increase rapidly with rising temperature. CO concentration in steam reforming of glycerol is much higher than in aqueous phase reforming of glycerol. At 250°C, CO concentration is 7400 ppm; at 500°C, it jumped to 0.9%. Hydrogen concentration maximizes when methane concentration minimizes to nearly zero at 550°C, which indicates that methane is converted to hydrogen and carbon monoxide via steam reforming.

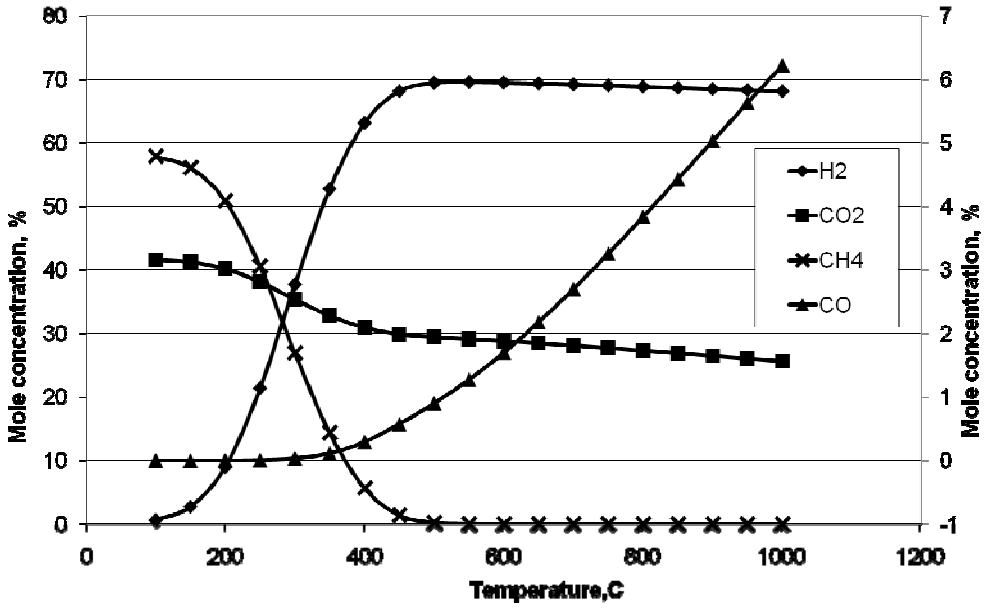


Figure 15. Equilibrium concentrations (water free base) of CO_2, H_2, CH_4 and CO in steam reforming of 10 wt% glycerol in water solution

Steam reforming of glycerol can produce small amount of hydrogen at low temperature (150^{o}C), however, hydrogen production maximizes only at temperature above 550^{o}C. Carbon monoxide concentration from steam reforming of glycerol is much higher than that is obtained from aqueous phase reforming. By comparison, hydrogen production from aqueous phase reforming is more attractive than from steam reforming due to its low temperature operation which can save energy and its low CO formation.

4.5 THERMODYNAMIC ANALYSIS OF THE WATER GAS SHIFT REACTION

One of the advantages of aqueous phase reforming of polyols to produce hydrogen is that in this process, the carbon monoxide concentration is reduced due to the mild reaction temperature (200^{o}C to 250^{o}C). Unlike steam reforming of natural gas, the temperature range for aqueous phase reforming of polyols also favors the forward water gas shift reaction. It is therefore possible to combine the reforming reaction with the water gas shift reaction in just one reactor. It is likely that the low level of CO in the aqueous phase reforming system is the benefit of the forward water gas shift reaction.

Thermodynamic analysis was carried out to investigate the water gas shift reaction and the equilibrium concentration of CO in the aqueous phase reforming of glycerol. A 10 wt% solution of glycerol in water was fed into a Gibbs reactor. The possible gas effluent from glycerol reforming includes H_2, CO_2, CO and hydrocarbons such as CH_4, C_2H_6 and C_3H_8 as well as water vapor. We then calculate the forward WGS equilibrium ratio (R) which is shown in equation 4.6 and defined as the ratio between the product of the concentration of CO_2 [CO_2] with H_2 [H_2] and the product of the concentration of CO [CO] with water vapor [H_2O].

$$H_2O + CO = CO_2 + H_2 \quad (2.2)$$

$$R = \frac{[CO_2] * [H_2]}{[CO] * [H_2O]} \quad (4.8)$$

Figure 16 shows the equilibrium constant for the water gas shift reaction. It is clear that the shift reaction is favorable at low temperatures; as system temperature increases, the equilibrium constant decreases. Previously in Chapter 4.2 the discussion of the change of Gibbs free energy for the water gas shift reaction also shows the same trend. From Figure 14, it is clear that CO generation is favorable at high temperatures; however, the CO concentration in the aqueous phase reforming of glycerol can be kept below 500 ppm under 250°C, the equilibrium limit for CO in the system under that temperature. The water gas shift reaction is the reason for the low concentration of CO in the gas product from aqueous phase reforming of glycerol.

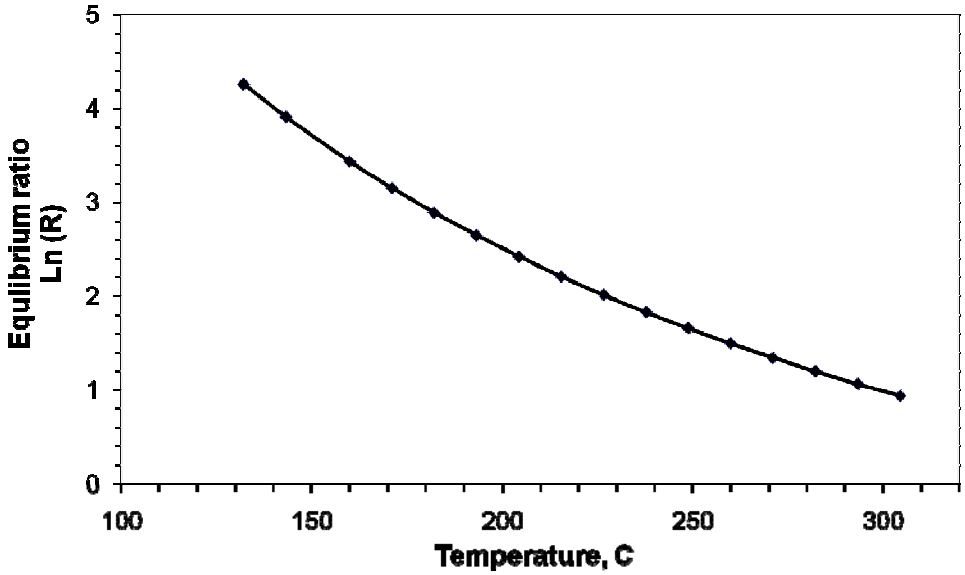


Figure 16. Equilibrium ratios for the WGS reaction in APR of 10 wt% glycerol

4.6 THERMODYNAMIC ANALYSIS OF SIDE REACTIONS

We have noted from thermodynamic calculations (Figure 14) that, as the temperature increases, the moles of CH_4 and CO_2 decrease with increasing moles of H_2 and CO. This can be attributed to side reactions such as methane steam reforming and methane dry reforming, which may occur to a very small extent under APR conditions.

$$CH_4 + H_2O = CO + 3H_2 \quad (2.1)$$

$$CH_4 + CO_2 = 2CO + 2H_2 \quad (2.7)$$

The equilibrium constants of steam reforming of methane and dry reforming of methane are defined as:

$$R_S = \frac{[CO] * [H_2]^3}{[CH_4] * [H_2O]} \quad (4.9)$$

$$R_D = \frac{[CO]^2 * [H_2]^2}{[CH_4] * [CO_2]} \quad (4.10)$$

These constants calculated from the aqueous phase reforming of 10 wt% glycerol are shown in Figure 17. It is clear that both steam reforming reaction and dry reforming of CH_4 reaction are favorable at high temperatures. Both CH_4 and CO are undesirable products; CH_4 competes with H_2 while CO could poison PEM fuel cells. In order to produce a high selectivity of H_2 with low amounts of CO, the temperature should be kept low (below 300^{o}C).

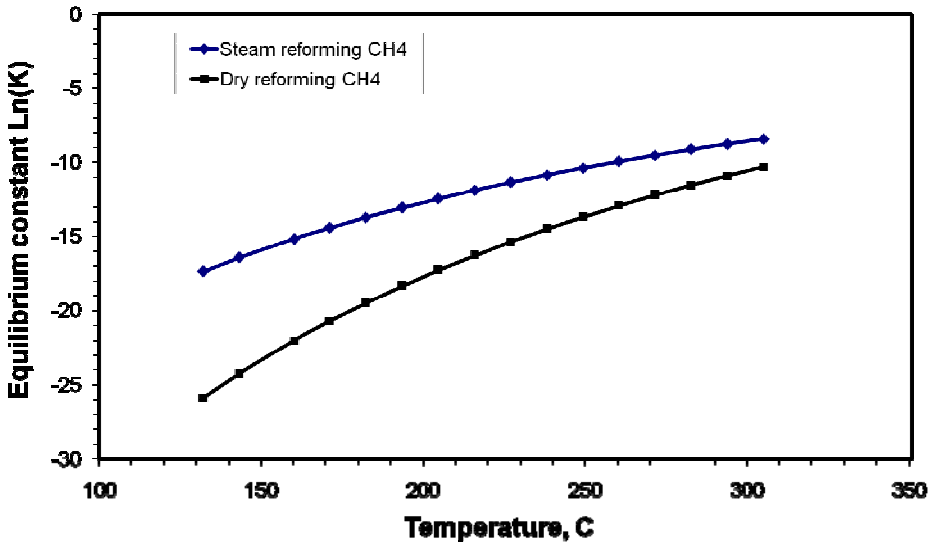


Figure 17. Equilibrium constants of steam reforming of CH_4 and dry reforming of CH_4 in the aqueous phase reforming of glycerol

4.7 CONCLUSIONS

We carried out a thermodynamic analysis to investigate hydrogen generation from low temperature aqueous reforming of glycerol and to compare it with steam reforming of methane. By setting the calculation pressure above the feed bubble point pressure at each temperature, the aqueous phase reforming conditions were resembled. It is clear that it is feasible to generate hydrogen via aqueous phase reforming of glycerol at much lower temperature than that for steam reforming of methane; CO formation is not favored at this low temperature range in the system

due to the water gas shift reaction. Calculations show that hydrogen generation from polyols with C:O ratio of 1:1 occurs at lower temperature than from other oxygenated hydrocarbons or alkanes with the same numbers of carbon atoms but less oxygen atoms. It also shows that addition of hydroxyl groups to the carbon chain makes the C-C bonds weaker so that the bonds in polyols are more readily broken than the C-C bonds in alkanes with the same number of carbon atoms. The numbers and positions of the hydroxyl groups in polyols affect the C-C bond energy. It not only shows that more hydroxyl groups bonded to the carbon chain cause a lower C-C bond energy, but also that the adjacent positions of the hydroxyl groups helps reduce the C-C bonds energy, leading to H_2 and CO_2 formation.

Thermodynamic analysis provides equilibrium composition of H_2, CO_2 and CH_4, the major gas products from aqueous phase reforming of glycerol. Other alkanes such as ethane and propane are negligible in the system, while the CO concentration is less than 500 ppm under 250^{o}C. As the temperature increases, the moles of H_2 and CO increase, while CO_2 and CH_4 decrease. The low concentration of CO in the system could be attributed to the water gas shift reaction, which converts most of CO to CO_2 and H_2 in the low temperature range. Some side reactions such as dry reforming of methane may occur in the system. Steam reforming of glycerol produces much more CO than from aqueous phase reforming; the temperature for maximum hydrogen generation is at 550^{o}C, a temperature much higher than the operation temperature of aqueous phase reforming of glycerol. Thermodynamic analysis shows that it is feasible to generate H_2 with very small amounts of CO via low temperature aqueous phase reforming of polyols. In the next chapter, we will discuss the selection of catalysts and kinetic studies of the process.

5.0 RESULTS AND DISCUSSION

5.1 APR OF ETHYLENE GLYCOL IN A BATCH SYSTEM

Aqueous-phase reforming of 10 wt% ethylene glycol solution was carried out in a 40 ml microautoclave at 220˚C. One half gram of platinum on alumina catalyst was loaded and reduced at 250^{o}C and 400 psi H_2 pressure. A 15 ml liquid solution of 10 wt% ethylene glycol in deionized water was introduced into the reactor with a syringe pump. The reaction was terminated after four hours. The gas product profiles are shown in Table 7. The pressure increase was 166 psi; the gas product contained over 99% of H_2 and CO_2, while CO constituted less than 0.1%. Liquid-phase products included small amounts of alcohols (methanol and ethanol), acetic acid and acetaldehyde.

The result showed that hydrogen with very small amounts of CO could be produced by the low temperature aqueous phase reforming of ethylene glycol. Therefore, a continuous fixed bed system was built to investigate hydrogen production through the aqueous phase reforming of polyols. The results are presented in the next section.

Table 7. Gas product distribution of ethylene glycol reforming in a batch system at 220°C

Gas Product	Concentration (%)
H_2	79.6
CO_2	20.3
CO	0.09
CH_4	0.08
C_2H_6	0.01

5.2 APR IN A CONTINUOUS SYSTEM

5.2.1 APR of ethylene glycol and of glycerol

In this study, 10 wt% of ethylene glycol or of glycerol in water solution were introduced into the continuous system at 0.1 ml/min. The weight hourly space velocity (WHSV) was 0.6 gram of glycerol per gram of catalyst per hour. One gram of catalyst was loaded in the reactor and reduced in H_2 flow (50 ml/min) at 250°C for two hours. At each temperature, the system pressure was kept slightly above the bubble point pressure to maintain the reaction in the liquid phase. The experimental results of aqueous phase reforming of ethylene glycol and of glycerol using 1% Pt/Al_2O_3 catalysts are shown in Tables 8 and 9, respectively. Here we use turnover frequency (TOF) which is defined as the number of H_2 molecules produced per active site per

unit time to compare the catalyst activity at different temperatures. The number of catalyst surface active sites was obtained from chemisorption tests. Similar to results obtained in the batch system, hydrogen and carbon dioxide are the major gas products from aqueous phase reforming of ethylene glycol or glycerol in the fixed bed continuous system. They constitute more than 99% of the gas from ethylene glycol reforming and more than 95% of the gas from glycerol with the rest being small amounts of gaseous alkanes (methane, ethane and propylene). We didn't detect CO in the ethylene glycol or glycerol reforming experiments. The CO detection limit of our gas chromatograph is 500 ppm. Carbon monoxide is therefore estimated to be less than 500 ppm from the aqueous phase reforming of ethylene glycol and of glycerol. Products in the liquid phase included small amounts of alcohols (methanol and ethanol), organic acids (acetic acid and glycolic acid, $HOCH_2COOH$), acetaldehyde and dissolved CO_2.

The hydrogen selectivity is defined as the number of hydrogen molecules detected in the effluent gas, normalized by the number of hydrogen molecules that would be present if the carbon atoms detected in the effluent gas molecules had all participated in the reforming reaction. Alkane selectivity is defined as the number of carbon atoms in the gaseous alkane products normalized by the total number of carbon atoms in the gaseous effluent stream.

$$\text{Hydrogen selectivity} = \frac{\text{Hydrogen produced in effluent gas}}{\text{Hydrogen could be produced if each carbon in the effluent gas participated in APR}} \times 100\% \quad (5.1)$$

$$\text{Alkane selectivity} = \frac{\text{Moles of carbon in alkanes}}{\text{Total moles of carbon in the effluent gas}} \times 100\% \quad (5.2)$$

It is assumed that in the stoichiometric reactions of reforming of ethylene glycol and of glycerol, each mole of ethylene glycol or of glycerol would yield 5/2 and 7/3 molecules of hydrogen, respectively. The reforming reactions were shown below.

$$C_2H_6O_2 + 2H_2O = 2CO_2 + 5H_2 \quad (5.3)$$

$$C_3H_8O_3 + 3H_2O = 3CO_2 + 7H_2 \quad (5.4)$$

Table 8. Experimental results of gas effluent from aqueous phase reforming of ethylene glycol

T (^oC)	220	250
P (psi)	385	625
Feed rate (ml/min)	0.1	0.1
WHSV (weight hourly space velocity)	0.6	0.6
H_2 (mol %)	70.1	68.3
CO_2 (mol %)	29.5	31.0
CH_4 (mol %)	0.3	0.5
C_2H_6 (mol %)	0.2	0.2
H_2 selectivity %	93.1	85.7
Alkane selectivity %	2.0	2.9
H_2 volumetric rate (ml/min)	8.1	15.4
Alkanes volumetric rate (ml/min)	0.058	0.158
Turnover frequency of H_2 (TOF) 1/min	12.6	23.9

*Aqueous phase reforming of 10 wt% of ethylene glycol over 1 g of Pt/Al_2O_3 (1 wt% Pt) catalyst, feed rate is 0.1 ml/min, WHSV is 0.6 gram of ethylene glycol per gram of catalyst per hour.

Table 9. Experimental results of gas effluent from aqueous phase reforming of glycerol

T (^{o}C)	220	250
P (psi)	385	625
Feed rate (ml/min)	0.1	0.1
WHSV (weight hourly space velocity)	0.6	0.6
H_2 (mol %)	61.7	61.9
CO_2 (mol %)	34.3	34.3
CH_4 (mol %)	3.7	3.4
C_2H_6 (mol %)	0.3	0.4
C_3H_8 (mol %)	0.03	0.05
H_2 selectivity %	68.3	68.6
Alkane selectivity %	11.3	11.3
H_2 volumetric rate (ml/min)	4.0	7.8
Alkanes volumetric rate (ml/min)	0.261	0.485
Turnover frequency of H_2 (TOF) 1/min	6.2	12.1

*Aqueous phase reforming of 10 wt% of glycerol over 1 g of Pt/Al_2O_3 (1 wt% Pt) catalyst, feed rate is 0.1 ml/min, WHSV is 0.6 gram of glycerol per gram of catalyst per hour.

The yield of hydrogen from ethylene glycol is higher than that from glycerol, and alkane production from reforming of ethylene glycol is less than that from reforming of glycerol. The hydrogen and alkane selectivities follow a similar trend. Hydrogen selectivity from ethylene

glycol is higher than that from glycerol at the same reaction temperature and pressure; while the alkane selectivity from ethylene glycol is lower than from glycerol at the same reaction conditions. At a temperature of 250°C, the hydrogen selectivity from reforming of ethylene glycol and of glycerol are 85.7% and 68.6%, respectively, while alkane selectivity from ethylene glycol and of glycerol are 2.9% and 11.3%, respectively. Aqueous phase reforming of ethylene glycol generated more hydrogen and fewer hydrocarbons than obtained from glycerol. At a temperature of 220°C, the hydrogen production rate from aqueous phase reforming of ethylene glycol is twice that from glycerol; while hydrocarbons from aqueous phase reforming of glycerol are 4.5 times more than from ethylene glycol. At a temperature of 250°C, hydrogen product rate from aqueous phase reforming of ethylene glycol is close to twice that from glycerol; while hydrocarbons from aqueous phase reforming of glycerol are 3 times more than from ethylene glycol. Increasing the temperature from 220°C to 250°C increases the hydrogen production rate 90% and 95% from aqueous phase reforming of ethylene glycol and glycerol, respectively; while alkane formation increases 170% and 86% from APR of ethylene glycol and glycerol, respectively.

The 1% Pt/Al_2O_3 catalyst is stable and active under the reaction conditions. It is also quite selective for H_2 production. Catalyst activity increases with temperature and deactivation was not observed at 250°C for 100 hours running. The catalyst is also used with other renewable polyols and their results are discussed in the next section.

5.2.2 APR of renewable polyols over Pt/Al_2O_3 catalysts

As discussed earlier, aqueous phase reforming is particularly suitable for the production of hydrogen from the less volatile polyols. It is difficult to obtain hydrogen from the nonvolatile polyols using steam reforming due to their high boiling points. We have succeeded in generating hydrogen from ethylene glycol and from glycerol; other biomass-derived polyols, such as glucose, sorbitol, mannitol and sucrose were also tested. Commercial products such as table sugar and corn syrup were included as potential hydrogen sources. Hydrogen production from those renewable polyols would have essentially zero-net greenhouse gas emissions and help realize the hydrogen economy. In this section, we discuss the aqueous phase reforming of a number of polyols for hydrogen production. All the results in Table 10 from aqueous phase reforming of polyols were obtained at 220^{o}C and polyol solutions were kept at 1 wt% in the experiments. Side reactions such as hydrocarbon and liquid organic formation occur in the APR of large polyols. All of the polyols generated hydrogen at a temperature around 220^{o}C. Aqueous phase reforming of glycerol produced the most hydrogen among the group. Glucose and corn syrup have the lowest hydrogen production capability by aqueous phase reforming in the group. The hydrogen production rate decreases in the order:

Glycerol > sucrose > mannitol ~ sorbitol ~ table sugar > glucose > corn syrup

Table 10. Experimental data for APR of different polyols

Polyols	H_2 (mol %)	CO_2 (mol %)	CH_4 (mol %)	H_2 selectivity %	Alkane selectivity %	H_2 rate (ml/min)
Glycerol	63.8	33.0	3.2	70.2	12.1	2.3
Sorbitol	59.7	35.8	3.5	66.3	13.9	1.2
Mannitol	59.5	37.0	2.6	65.9	11.1	1.3
Glucose	52.2	42.6	3.5	52.1	14.9	0.5
Sucrose	51.9	37.4	8.0	62.3	28.0	1.5
Table sugar	58.3	34.8	4.76	66.6	17.7	1.1
Corn syrup (97% D-glucose)	14.1	83.1	1.7	8.1	4.9	0.03

*Aqueous phase reforming of polyols over 1 g of Pt/Al_2O_3 catalyst at 220^{o}C, feed rate kept at 0.1ml/min and WHSV is kept at 0.6 g of polyol per g of catalyst per hour.

As the number of carbon atoms in the polyol increases, hydrogen selectivity generally decreases. Glycerol showed the highest hydrogen selectivity while corn syrup has the lowest. The trend may be a result of the increasing number of side reactions resulting from a large number of intermediates from the more complicated polyols, posing a challenge for hydrogen selectivity. Aqueous phase reforming of table sugar produced more hydrogen and showed higher selectivity than did corn syrup. Selectivity for hydrogen production improves in the order:

Corn syrup < glucose < sucrose < mannitol ~ sorbitol ~ table sugar < glycerol

The effect of temperature on hydrogen and alkane selectivities from the APR of several different polyols is shown in Figure 17. As temperature increases, hydrogen selectivity from different polyols, as shown by symbol (♦ for 220^{o}C and ■ for 250^{o}C) decreases while alkane selectivity, as shown by symbol (▲ for 250^{o}C and ● for 220^{o}C) increases. High hydrogen selectivities (more than 60%) are obtained from ethylene glycol, glycerol, sorbitol, mannitol, sucrose and table sugar but not from glucose and corn syrup as the feedstock. The more immediately available polyols, such as glucose, corn syrup, sucrose and sugar may be more practical and interesting if they can be converted to hydrogen via low temperature aqueous phase reforming reactions. Alkane selectivity follows a trend opposite to that of hydrogen selectivity. Mannitol and sorbitol are isomers with a different position of one hydroxyl group; however aqueous phase reforming of mannitol produced essentially the same amount of hydrogen as sorbitol did. The position of OH groups does not affect the amount of hydrogen production in aqueous phase reforming. Figure 18 shows that higher temperatures favor alkane formation over hydrogen formation, while lower temperatures follow the opposite trend. Increased temperature generally increases catalyst activity, as shown for glycerol. However, we did not observe activity increases from the other polyols; moreover, catalyst deactivation occurred in the aqueous phase reforming of glucose and sucrose at high temperature (above 250^{o}C). For the long chain polyols (with six carbon atoms), the temperature should be kept below 250^{o}C.

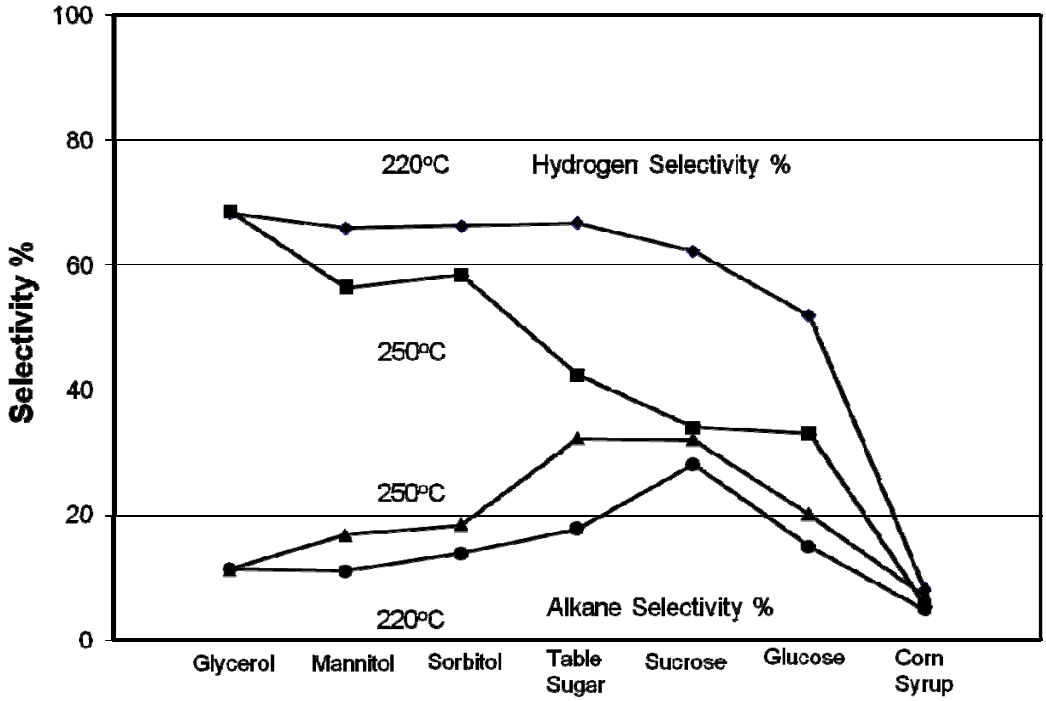


Figure 18. Hydrogen and alkane selectivity from APR of different polyols over 1 wt% Pt/Al_2O_3 catalyst at temperature 220°C and 250°C

Carbon monoxide was not detected from the APR of ethylene glycol, glycerol or sorbitol. It was detected from glucose and sucrose at a higher temperature (250°C). We estimated that CO in the gas stream was less than 500 ppm at 220°C. Organic compounds detected in the liquid phase from the long chain polyols (sorbitol, glucose and sucrose) include methanol, ethanol, propanol, acetic acid, propionic acid, acetone and formaldehyde.

5.2.3 APR of polyethylene glycol over Pt/Al_2O_3 catalysts

We tested the aqueous phase reforming of the polymer, polyethylene glycol (PEG-200) for hydrogen production. PEG-200 is a polymer with an average molecular weight of 200, its formula is $(CH_2CH_2O)_{n,}$ with a range of n from 2 to 6. In this study, 10wt% of polyethylene glycol in water solution was introduced into the continuous system at 0.1 ml/min. The weight hourly space velocity (WHSV) was 0.6 gram of polyethylene glycol per gram of catalyst per hour.

Table 11. Hydrogen production from ethylene glycol, glycerol and polyethylene glycol

Reactant compound	H_2 production rate ml/min	
	T = 220°C , P = 385 psi	T = 250°C, P = 625 psi
Ethylene glycol	8.1	15.4
Glycerol	4.0	7.8
Polyethylene glycol	1.1	2.5

*Aqueous phase reforming of ethylene glycol, glycerol and polyethylene glycol (all 10 wt%) over 1 g Pt/Al_2O_3 (1 wt% Pt) catalyst

Polyethylene glycol did not produce as much hydrogen as ethylene glycol and glycerol did, as shown in Table 11. At 220°C and 385 psi reaction conditions, polyethylene glycol produced hydrogen at 1.1 ml/min; at 250°C and 625 psi, polyethylene glycol produced hydrogen

at 2.5 ml/min. Because of the long chain polymer ether structure, it had more intermediates in the liquid, as shown from the mass spectroscopic chromatogram Figure 19. Compared with the GCMS image of the 10 wt% PEG-200 in water solution before reaction (Figures 3.6), it is clear that the long chain polymer decomposed to small units, peaks for the last three either disappeared or decreased.

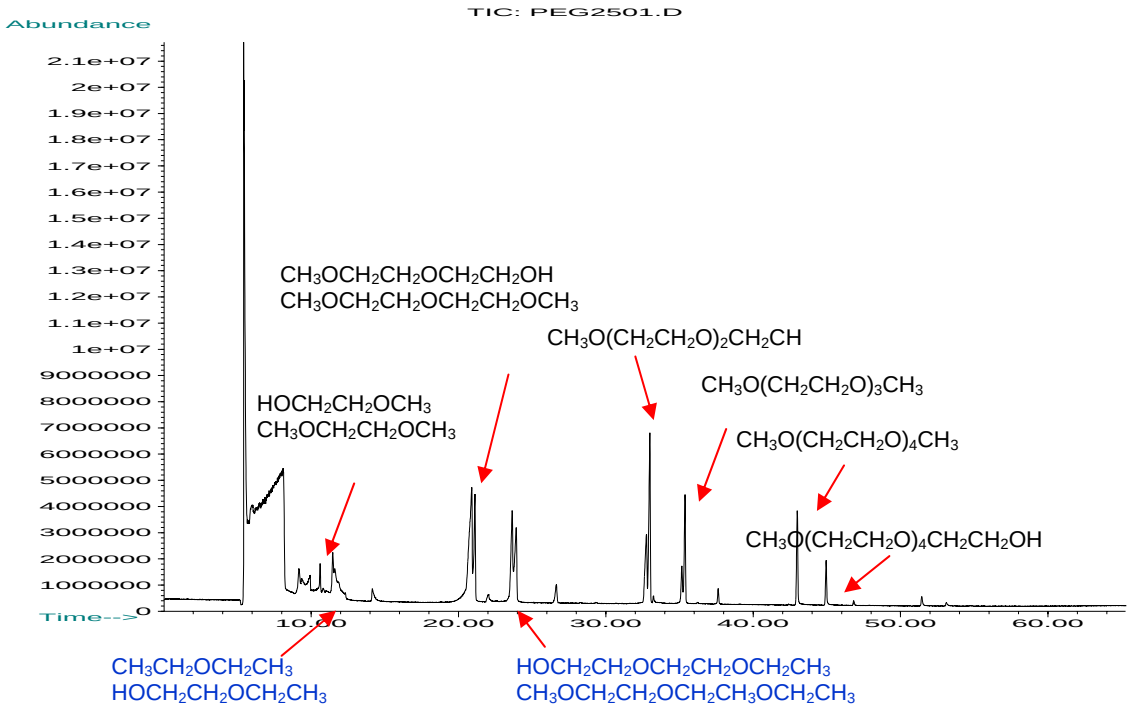


Figure 19. GCMS image of 10 wt% PEG-200 in water solution after reaction

5.3 CATALYST CHARACTERIZATION

In this section, the results of characterization of catalysts are presented, which include physical property tests (BET surface area and pore size distribution) and surface chemical properties (CO chemisorption test and transmission electron microscopy).

5.3.1 BET and Chemisorption

The BET surface area and pore properties of the catalysts were characterized through an Accelerated Surface Area and Porosimetry (ASAP) system, ASAP 2010, from Micromeritics Instrument Corporation. A small amount of catalyst sample, about 0.2 g, was weighed and loaded into a sample tube. After putting a filler rod inside the tube, the opening of the sample tube was blocked with a seal frit. Then the sample was degassed under vacuum at 90°C for 1 hour and then at 350°C till the pressure was less than 10 μmHg. There is a cold trap with liquid nitrogen for elimination of moisture in the degas system. After cooling and backfilling with nitrogen, the sample tube assembly was weighed and the precise weight of the sample calculated by subtracting the weight of the empty tube assembly. Physisorption with nitrogen was carried out in an insulated liquid nitrogen bath, at about -196°C. The adsorption and desorption isotherms were then obtained automatically using the software of ASAP 2010 for Windows®, v. 4.01 Beta.

The metal dispersion is the percentage of active metal atom (as detected by carbon monoxide adsorption) in the total amount of metal atom on the surface of support. We used a Micromeritics® ASAP 2010 System manufactured by Micromeritics Instrument Corporation to measure Pt dispersion of the catalysts. For each experiment, a catalyst sample was weighed and

loaded in a U-shape quartz sample tube. Prior to carbon monoxide adsorption, the catalyst was reduced in flowing hydrogen at 350°C for 1 hour. After reduction, hydrogen was evacuated and sample was kept at 350°C for another 90 minutes and then cooled down to 35°C. The adsorbent was then added to catalyst 10 times until the equilibrium pressure was reached. The gas in the tube was then evacuated for 30 minutes at 35°C to a pressure of 10^{-6} Torr. After evacuation, the adsorbent was again added to the sample to determine the amount of reversibly adsorbed carbon monoxide. The irreversible uptake was determined from the difference between two isotherms. The surface area (m^2/g sample) of Pt was also measured in the same process. Characteristics of the Pt based catalysts (BET and Chemisorption test results) used in the aqueous phase reforming of polyols for hydrogen productions are summarized in Table 12.

Table 12. Characterization of Pt based catalysts

Catalysts	BET Surface area m^2/g	Pore size (Diameter) A	Metal dispersion %	Metal surface area m^2/g catalyst	Metal surface area m^2/ g metal
Pt/Al_2O_3 0.3% Pt	141.8	56	55.5	0.41	137.0
Pt/Al_2O_3 1% Pt	133.1	58	56.3	1.39	139.2
Pt/Al_2O_3 5% Pt	129.2	70	40.0	4.94	98.7

The BET results show that Pt based catalysts with a Pt loading from 0.3 to 5% have an average surface area of 134.7 m^2/g. Under low metal loading conditions (equal or less than 5% Pt loading), BET surface area of the catalysts is more dependent on the support. BET surface area of the catalysts is close to the support surface area. γ-Al_2O_3 (from Aldrich Chemical Inc.) has a surface area of 155 m^2/g and pore size diameter of 58 A. Catalyst with a higher Pt loading has a lower surface area but a bigger pore size. Catalyst with a lower Pt loading has a higher Pt metal dispersion, leading to a higher metal surface area. The Pt dispersion of 1 % Pt/Al_2O_3 and 5% Pt/Al_2O_3 catalyst is 56.3% and 40%, respectively. Although more Pt metal is loaded on the support, a lower percentage of Pt is active.

Table 13. Comparison of Pt/Al_2O_3 with different Pt loading

Catalysts	BET Surface area m^2/g	Metal Dispersion (%)	TOF of H_2 (min^{-1})
Pt/Al_2O_3 0.3% Pt	141.8	55.5	12.6
Pt/Al_2O_3 1% Pt	133.1	56.3	12.1
Pt/Al_2O_3 5% Pt	129.2	40.0	5.7

*Aqueous phase reforming of 10 wt% glycerol at 250^oC and 625 psi pressure, feed rate is 6 ml/h

In Table 13 the Pt/Al_2O_3 catalysts with a 0.3% and 1% metal loading have a similar metal dispersion and a close turnover frequency of H_2 production. However, the Pt/Al_2O_3 catalyst with a 5% Pt loading has a lower metal dispersion and a lower turnover frequency of H_2 production. The results indicate that H_2 production over 5% Pt/Al_2O_3 catalyst were limited by transport phenomena and fall in the diffusion regime; an absence of transport limitation for the Pt/Al_2O_3 catalysts with a 0.3% and 1% metal loading was satisfied. For the high loading platinum catalyst (5 wt%), the transport limitations can be overcome by reducing the catalyst particle size or by increasing the feed flow rates to reduce the diffusion effect.

5.3.2 Surface Features Measured by TEM

Transmission electron microscopy images of the catalyst surface were obtained using a JEOL 2000FX STEM system, which has a line resolution of 0.14 nm. The JEOL 200CX is equipped with a tungsten filament, capable of conventional diffraction contrast imaging, selected area diffraction, and magnetic domain imaging by Lorentz TEM. The JEOL 2000FX features analytical TEM attachments for thin window EDS and electron energy-loss spectroscopy (EELS) with energy resolution of about 2eV for compositional and chemical characterization from areas as small as ~15nm. In scanning TEM (STEM) mode, bright-field and dark-field imaging and the collection of both EDS and EELS profiles or maps is possible with the Emispec Vision system that can control all data channels simultaneously.

Catalyst samples were suspended in ethanol solution. After ultrasonic treatment, slurry of the solution was dropped onto the copper grid, which was used to hold small sample particles. The sample was placed into the testing chamber after evaporation of ethanol. A 200kV transmission electron was used to generate TEM images. In addition to the TEM test, energy

dispersive x-ray analysis (EDX) analysis was used with the same setup to identify the major element distribution of any spot over the sample. Using EDX, we can identify the composition of particles of interest on a TEM image. Pt catalyst synthesis results in nanocomposite materials. Figure 20 shows the TEM image of 1% Pt/Al_2O_3 catalyst, where metal Pt nanoparticles (shown as the dark black dots) with average particle size of about 5 nm and narrow size distributions are embedded in support Al_2O_3. The materials are characterized by an irregular, porous structure with a homogeneous distribution of Pt metal in Al_2O_3.

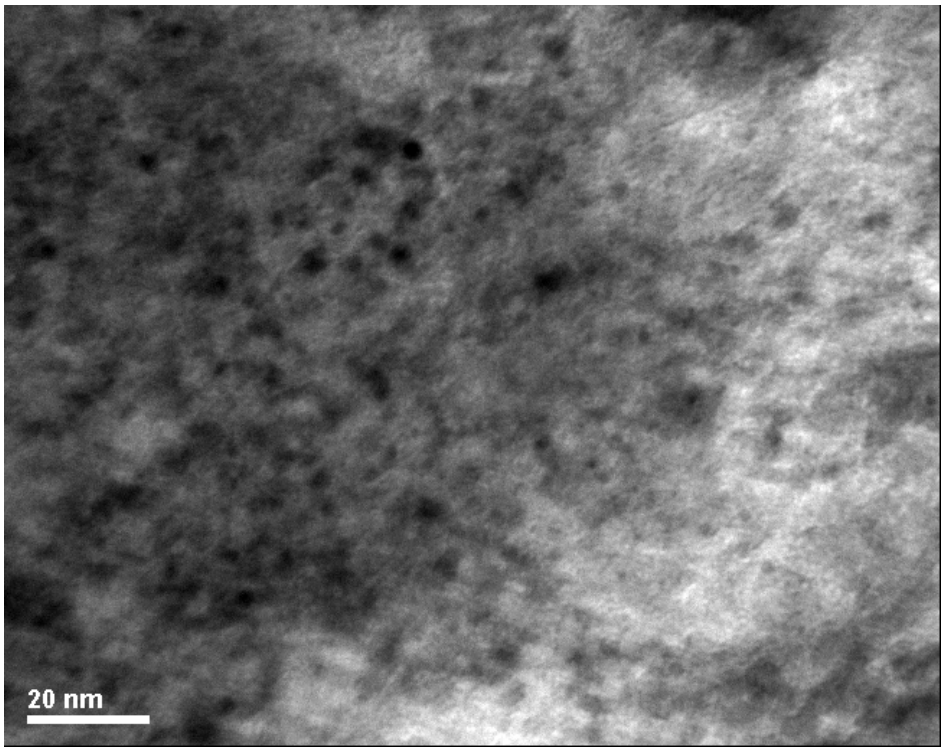


Figure 20. TEM image of 1% Pt/Al_2O_3 catalyst

5.4 DISCUSSION

5.4.1 Catalyst selection

5.4.1.1 Catalyst metal

As discussed earlier, aqueous phase reforming of polyols for hydrogen production involves the breakage of the C-C and C-O bond on the catalyst surface with rearrangements leading to formation of intermediates which may react with water to form hydrogen. It has been pointed out that group VIII metals generally show high activities for C-C bond breakage [53]. In this study, alumina supported group VIII metal (Ru, Pt and Pd) catalysts were tested in the aqueous phase reforming of 10 wt % of glycerol solution at a temperature of 250^{o}C and a pressure of 625 psi; the hydrogen and alkane selectivity as well as hydrogen and CO yield are shown in Table 14. Pt, Pd and Ru catalysts have the same metal loading of 5%.

Table 14. Results for APR of glycerol over alumina supported metal catalysts

Catalysts	Metal loading %	H_2 selectivity %	Alkane selectivity %	H_2 production rate ml/min	CO production rate ml/min
Pt/Al_2O_3	5	66.4	15.7	15.8	0
Ru/Al_2O_3	5	7.6	57.6	1.6	0
Pd/Al_2O_3	5	38.7	11.2	2.2	1.1

*Aqueous phase reforming of 10 wt% glycerol solution at 250^{o}C and 625 psi

Among the four alumina supported group VIII metal catalysts, the highest activity is exhibited by Pt/Al_2O_3, as shown by the hydrogen production rate and selectivity. At 250°C and 625 psi, the hydrogen production rate using the platinum catalyst was 15.8 ml/min with a 66.4% hydrogen selectivity. At the same time CO production from the platinum catalyst was the lowest among the four alumina supported catalysts. The catalyst activity in aqueous phase reforming of glycerol over alumina supported metal catalysts at a temperature of 250°C (as measured by H_2 production rate) decreases in the order:

$$Pt/Al_2O_3 > Pd/Al_2O_3 > Ru/Al_2O_3$$

With glycerol, Pd can produce fair amounts of H_2 and has low alkane selectivity; but it favors CO formation under the conditions of the experiment. Pd/Al_2O_3 produced the highest amount of CO. Ru has the poorest activity for H_2 production; its low H_2 selectivity is due to its inclination to alkane formation; indeed, Ru has the highest alkane selectivity in the APR of glycerol.

The H_2 selectivity for aqueous phase reforming of 10 wt% glycerol over alumina supported group VIII metal catalysts, tested at temperature of 250 °C, decreases in the order:

$$Pd/Al_2O_3 > Pt/Al_2O_3 > Ru/Al_2O_3$$

While the alkane selectivity decreases in the order:

$$Ru/Al_2O_3 > Pt/Al_2O_3 > Pd/Al_2O_3$$

5.4.1.2 Catalyst support

This section deals with the choice of supports for Pt in the APR of glycerol for hydrogen generation. Pt catalysts were prepared on supports TiO_2, SiO_2, MgO, ZrO_2 and Al_2O_3 by incipient wetness impregnation methods. The Pt metal loading was 1wt% for each catalyst. Aqueous phase reforming of 10 wt% glycerol in water solutions with these catalysts produced

primarily H_2 and CO_2. All the catalysts were tested at three different temperatures: 220°C, 250°C and 280°C. For each temperature, the system pressure was kept slightly above the solution bubble point pressure in order to keep it in the liquid phase and the system was held for about 10 hours to reach a steady state. The system was then heated to next temperature point at a slow heating ramp of 0.5°C/min in order to prevent temperature fluctuation. The feed rate of glycerol solutions was kept at 6 ml/h.

In addition to H_2 and CO_2, all catalysts generated small amount of hydrocarbons (mostly methane) and organic byproducts such as ethanol, acetaldehyde and acetic acid in the liquid. CO was not detected in these experiments due to GC limitation but was estimated to be below 500 ppm. The volumetric rates for H_2, CO_2 and CH_4 production are shown in Figure 21.

The results show that Pt/Al_2O_3 has the highest hydrogen production rate from APR of glycerol at all temperatures from 220°C to 280°C. Pt/MgO, Pt/SiO_2 and Pt/TiO_2 show medium activity for APR of glycerol to produce H_2, whereas low catalytic activity is observed from Pt/ZrO_2 catalyst. The supported Pt catalysts can be ranked in the following order with respect to the volumetric H_2 production rate:

$$Pt/Al_2O_3 > Pt/SiO_2 \sim Pt/TiO_2 \sim Pt/MgO > Pt/ZrO_2$$

As the temperature increases, the Pt catalyst activity (measured by the volumetric H_2 and CO_2 production rate) increases and so does the byproduct CH_4 formation rate. Catalyst deactivation was observed only on the Pt/ZrO_2 catalyst after about 15 hours. Alumina supported platinum catalyst has the highest activity for the aqueous phase reforming of glycerol to produce hydrogen; it was the primary catalyst used to investigate hydrogen production from glycerol and other renewable polyols.

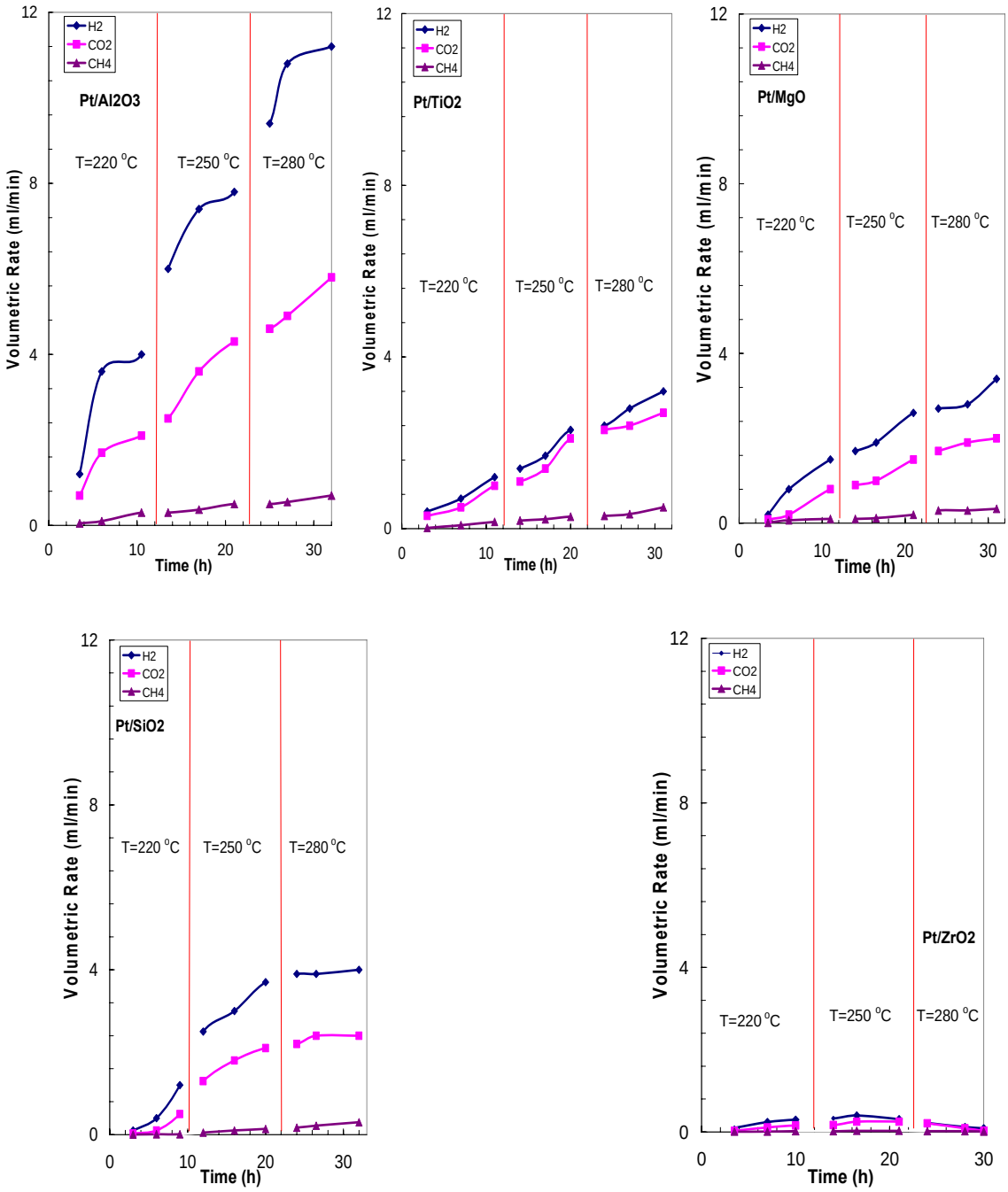


Figure 21. Hydrogen rate from aqueous phase reforming of glycerol over Pt/Al_2O_3, Pt/TiO_2, Pt/MgO, Pt/SiO_2 and Pt/ZrO_2 catalyst

5.4.2 Effect of polyol structure on H_2 production

As mentioned earlier, reforming polyols to produce CO_2 and H_2 is thermodynamically more favorable than the reforming of alkanes with the same number of carbon atoms at the same temperatures. The following is a discussion of the effect of polyol structure, i.e. the number and the position of hydroxyl and alkyl groups as well as chain length, on hydrogen production by aqueous phase reforming of polyols and related compounds.

5.4.2.1 Effect of the number and the position of hydroxyl groups

In Chapter 4.2 thermodynamic calculations indicated that addition of hydroxyl groups to the carbon chain makes the C-C bonds weaker so that the bonds in polyols are more readily broken than the C-C bonds in alkanes with the same number of carbon atoms. More hydroxyl groups bonded to the carbon chain cause a lower C-C bond energy; and adjacent positions of the hydroxyl groups helps reduce the C-C bonds energy, leading to H_2 and CO_2 formation. Experiment results were provided in this section to investigate the effect of the number and the position of hydroxyl groups on hydrogen production from APR of polyols. We compared hydrogen production from the aqueous phase reforming of 1-propanol, 1,2-propanediol, 1,3-propanediol and glycerol. Each compound has three carbon atoms but the number and position of the hydroxyl groups vary. 1,2-Propanediol and 1,3-propanediol share the same numbers of hydroxyl groups but they are in different positions in the chain. 10 wt% of alcohol or polyols solutions were introduced into the continuous system to generate hydrogen. The results at a temperature of 270^{o}C and a pressure of 850 psi are presented in Table 15.

It is found that, at the same temperature and pressure, compounds with more hydroxyl groups bonded to carbon atoms yield more hydrogen. 1-Propanol gave the lowest hydrogen

yield and produced more hydrocarbons than glycerol, mostly ethane. 1,3-Propanediol also produced a high level of hydrocarbons, mostly ethane, while the hydrocarbons produced from glycerol and 1,2-propanediol were mostly methane, which indicates that the C-C bond scission in 1,2-propanediol occurs in both C-C chain and leads to formation of methane while C-C bond scission in 1,3-propanediol occurs mostly in just one of the C-C chain and leads to formation of ethane. This is also the reason why 1,2-propanediol yielded more H_2 and fewer hydrocarbons than did 1,3-propanediol. At the same temperature and pressure, it appears that polyols with adjacent hydroxyl groups yield more hydrogen on APR.

Table 15. Gas product component and hydrogen yield from ethylene glycol, glycerol, 1-propanol 1,2-propanediol and 1,3-propanediol

	H_2 %	CO_2%	Total hydrocarbon%	H_2 rate (ml/min)
Ethylene glycol $HOCH_2$-CH_2OH	66.8	31.8	1.4	15.9
Glycerol $HOCH_2$-CHOH-CH_2OH	61.5	33.3	5.2	7.7
1,2-Propanediol $HOCH_2$-CHOH-CH_3	58.9	30.7	10.4	4.1
1,3-Propanediol $HOCH_2$-CH_2-CH_2OH	46.5	32.6	20.9	3.4
1-Propanol $HOCH_2$-CH_2-CH_3	45.4	26.6	28.0	3.2

*Aqueous phase reforming of 10 wt% polyols in water solution with a feed rate of 0.05 ml/min over 1 g Pt/Al_2O_3 (1 wt% Pt) catalyst at 270^o C and 850 psi.

5.4.2.2 Effect of introduction of an alkyl or methylene group to ethylene glycol

We compared ethylene glycol with 1,2-propanediol and 1,3-propanediol, in which a methyl group or a methylene group is added to the ethylene glycol molecule. The gaseous composition and H_2 production rate from aqueous phase reforming of these polyols at 270^{o}C and 850 psi are shown in Table 15.

It is found that aqueous phase reforming of ethylene glycol produces more hydrogen and much less hydrocarbons than APR of either 1,2-propanediol or 1,3-propanediol. There is a slight difference between 1,2-propanediol and 1,3-propanediol in regard to hydrogen and hydrocarbon formation when they are compared with ethylene glycol. Aqueous phase reforming of both 1,2 and 1,3-propanediol formed more intermediates, leading to methane or ethane instead of carbon dioxide and hydrogen.

5.4.2.3 Effect of chain length of polyols

It seems that higher yields of hydrogen are obtained from compounds that contain a hydroxyl group on every carbon. Glycerol has three hydroxyl groups and perhaps would be expected to yield more hydrogen than ethylene glycol. But ethylene glycol gave more hydrogen and fewer hydrocarbons at the same temperature and pressure. As C-C bond breakage is the main pathway in aqueous-phase reforming, polyols with long chain of carbon atoms will give more intermediates, producing more hydrocarbons and lowering H_2 yield.

5.4.3 Kinetic studies of aqueous phase reforming of glycerol and ethylene glycol over Pt/Al_2O_3

In this section, we report on reaction kinetic studies to investigate the effect of conditions such as temperature, pressure and feed concentration on hydrogen selectivity and yield from the APR of glycerol and ethylene glycol.

5.4.3.1 Temperature effect

Reaction rates depend strongly upon the reaction temperature. Increasing temperature results in an increase in reaction rate for most reactions. The Arrhenius equation can be used to correlate the relation between the rate constant and temperature. A is the frequency factor or the probability of occurrence of the reaction and Ea is the activation energy.

$$k = A\, e^{-Ea\,/\,RT} \tag{5.5}$$

Converting the Arrhenius equation into logarithmic form, we have:

$$\ln k = \ln A - E_a / \mathrm{RT} \tag{5.6}$$

Aqueous phase reforming of ethylene glycol and of glycerol over 1 wt % Pt/Al_2O_3 catalyst at different temperatures was carried out and the reaction rates were measured. Ethylene glycol and glycerol concentrations (1wt%) and feed rate (0.01 ml/min) were kept at low levels. Analysis of APR reaction data is complicated by the fact that pressure and temperature strongly interact due to changes in solubility of CO_2 and H_2. To minimize evaporation of water and

changes of solubility of CO_2 and H_2, we use a pressure 50 psi higher than the bubble point pressure. It is assumed that the system pressure consists of the vapor pressure of water at a certain temperature and the partial pressures of the products (mostly hydrogen and carbon dioxide). Therefore, the sum of hydrogen partial pressure and carbon dioxide partial pressure remained constant (50 psi) at each temperature. Measurements of the hydrogen production rates were made at different temperatures, data is in Appendix Table 26. By fixing the glycerol feed concentration as well as the sum of hydrogen and carbon dioxide partial pressure, we assume that hydrogen production rate is only a function of temperature. A plot of ln(k) versus 1/T yields a straight line with a slope –Ea/R and an intercept ln A. The turnover frequency of hydrogen is plotted versus the reciprocal of temperature (1/T) in logarithmic coordinates. The results of these experiments are shown in Figure 22. A straight line is a good fit for the data and can be used to calculate an apparent activation energy of 90 kJ/mole for ethylene glycol and 132 kJ/mol for glycerol, which suggests that hydrogen production from ethylene glycol is easier than from glycerol. The activation energy for ethylene glycol from our data agrees fairly well with the value of 101 kJ/mole reported by Shabaker's for conversion of ethylene glycol using a 0.59 wt% Pt/Al_2O_3 catalyst [43].

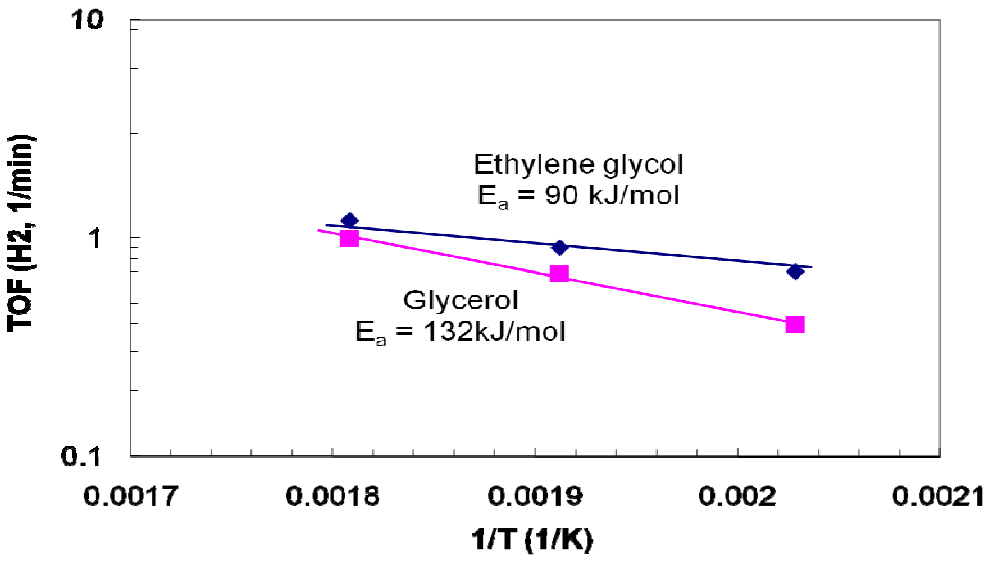


Figure 22. Plot of turnover frequency of H_2 versus reciprocal temperature for APR of ethylene glycol (1wt%) and of glycerol (1wt%) at temperature 220°C, 250°C and 280°C, with a feed rate of 0.01min/min

5.4.3.2 Pressure effect

System pressure, used to control the phase of the reaction zone, is an important parameter in aqueous phase reforming. The reaction rate can be expressed as a function of pressure as:

$$\gamma\,(_{TOF}) = C\,P^{b} \qquad (5.7)$$

where C and b are constants. Cnverting the equation into logarithmic form, we have:

$$\ln(\gamma) = \ln(C) + b \ln(P) \quad (5.8)$$

A plot of ln (γ) versus ln (P) is a line with a slope b and an intercept ln (C).

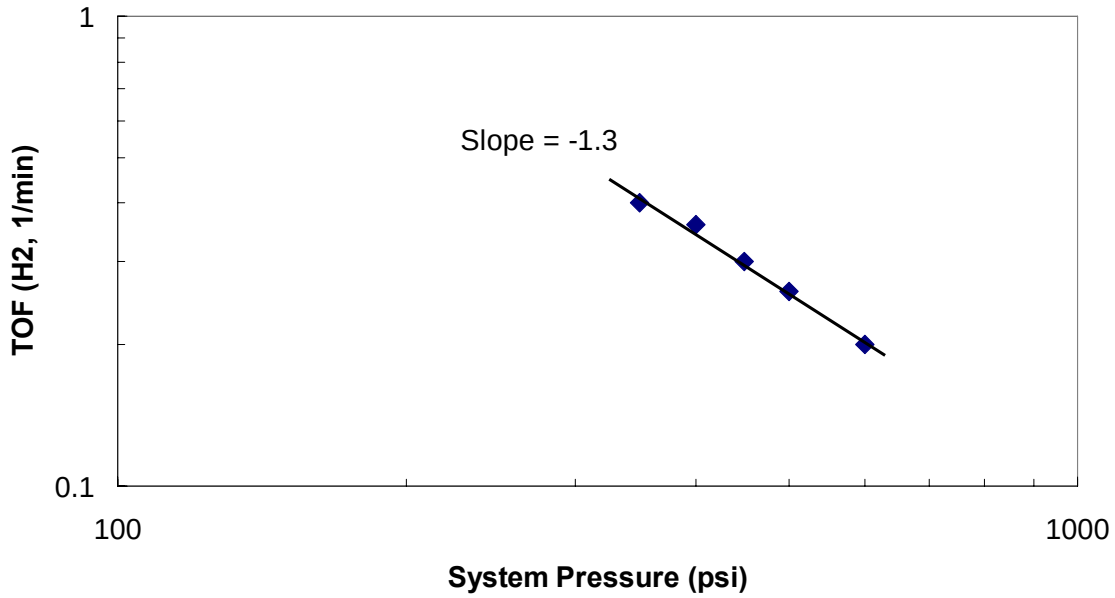


Figure 23. Plot of hydrogen turnover frequency versus system pressure for APR of 1 wt% glycerol over 1 wt% Pt/Al_2O_3 catalyst at 220°C with a feed rate of 0.01 ml/min

To study the effect of pressure, other parameters such as temperature and feed concentrations should be fixed, so that only pressure changes. Aqueous phase reforming of 1 wt% glycerol solution over 1 wt % Pt/Al_2O_3 catalyst were carried out at 220°C and 350 psi pressure. Without changing the temperature, the pressure was increased from 350 psi to 600 psi

at 50 psi intervals and the reaction rate was measured at each pressure. All the pressures were above the bubble point pressure, so that the reaction was kept in the aqueous phase. The feed concentration (1wt %) and feed rate (0.01 ml/min) were kept low. The turnover frequency of H_2 was used to measure rate and plotted versus pressure in logarithmic coordinate in Figure 23; data is in Appendix Table 27.

It is clear that system pressure strongly inhibits aqueous phase reforming of glycerol at 220^{o}C. The regression of TOF versus pressure gives a straight line with a slope of -1.3. Pressure inhibition of hydrogen production probably derives from the fact that increasing the system pressure at constant temperature increases the partial pressures of the products in the gas (i.e., H_2 and CO_2); the increased H_2 and CO_2 partial pressures would increase solubility and could inhibit H_2 production and might result in the formation of methane, which lowers the H_2 production rate. It should be emphasized that pressure changes are significant over the range of temperatures used. Analysis of APR reaction data is complicated by the fact that pressure and temperature strongly interact due to changes in solubility of CO_2 and H_2 with pressure and temperature. Since CO_2 and H_2 are desired products, and the reaction takes place in the liquid phase, rapid removal of products favors the reaction. Operation at as low a pressure as possible is favorable, thus establishing the bubble point of the mixture at the temperature as the minimum pressure. Operation at higher pressures retards the desired reaction and increases undesired side reactions. Therefore, in order to get a high hydrogen production rate, the system pressure should be kept low and still slightly above the bubble point pressure.

5.4.3.3 Feed concentration effect

Reaction rate is expressed in the form of reactant concentration. We carried out the aqueous phase reforming of glycerol over 1 wt% Pt/Al_2O_3 at 220^oC, and with glycerol concentration changing from 1 wt % to 10 wt %. Temperature and pressure were fixed, so that only the feed concentration changed. Both the solution concentrations (less than 10 wt %) and the feed rate (0.01 ml/min) were kept low. Measurements of the turnover frequency of hydrogen were made at feed concentration of 1 wt%, 5 wt% and 10 wt%. The turnover frequency is plotted versus feed concentration in logarithmic coordinates in Figure 24; data is in Appendix Table 28.

A plot of the turnover frequency of hydrogen production presents a straight line with a slope of 0.37. The rate of aqueous phase reforming of glycerol reaction is a fractional order with respect to the concentration of glycerol in water solution. The low reaction order may be due to changes in the catalyst surface coverage by adsorbed species derived from glycerol under the low temperature conditions. Increasing the temperature or feed concentration may overcome the low order kinetics.

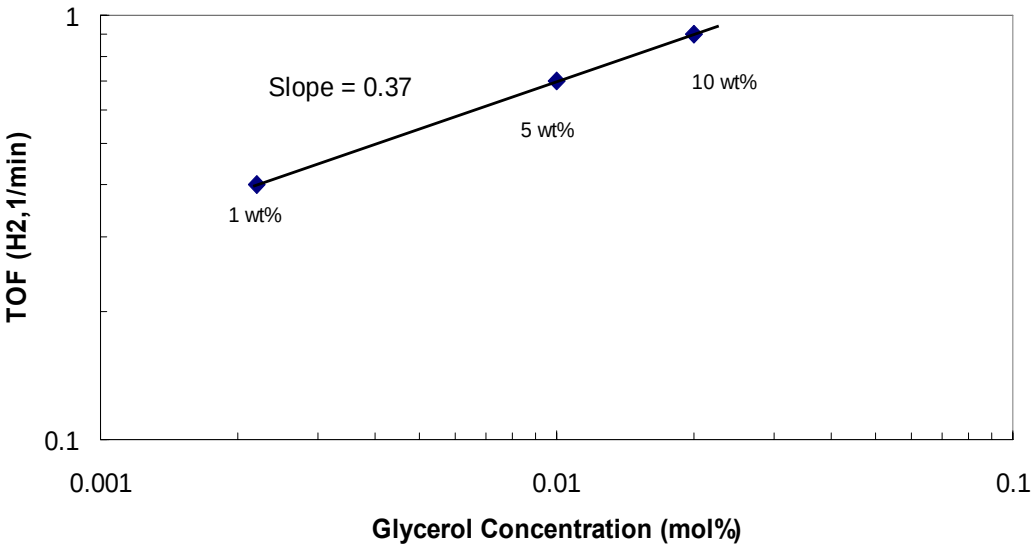


Figure 24. Plot of turnover frequency of H_2 versus feed concentration for APR of glycerol over 1 wt% Pt/Al_2O_3 catalyst at 220°C and 385 psi with a feed rate of 0.01 ml/min

5.5 CONCLUSIONS

It is demonstrated in our studies that hydrogen containing low level of carbon monoxide can be produced in a low temperature, single reactor process from a variety of polyols. Pt/Al_2O_3 catalysts exhibited good activity for hydrogen production while maintaining low formation of alkanes and carbon monoxide. We found the numbers and positions of OH groups affected hydrogen production from aqueous phase reforming and long chain polyols produced more intermediates than small polyols, leading to lower hydrogen selectivity. Studies were carried out to investigate the effect of temperature, pressure and feed concentrations on hydrogen yield and

selectivity. This is the first time, to our knowledge, that detailed data for hydrogen production from glycerol has been reported. The fact that no CO was detected in the gas product from APR of ethylene glycol and of glycerol indicates that the water gas shift reaction is an important aspect because it removes CO from the Pt catalyst surface and prevents adsorbed CO from blocking the surface active sites. Higher temperature results in higher hydrogen yields; the aqueous phase reforming of ethylene glycol has a lower apparent activation energy barrier than that of glycerol. The aqueous phase reforming reaction is strongly inhibited by system pressure. In order to get a high hydrogen yield, the system pressure should be kept slightly above the bubble point pressure. Aqueous phase reforming of glycerol has low order kinetics in dilute glycerol solutions at low temperatures, which may be due to the poor catalyst surface coverage by adsorbed species derived from glycerol under such conditions.

6.0 VALUABLE CHEMICALS FROM BIOMASS DERIVED POLYOLS

6.1 INTRODUCTION

Biomass can not only provide fuel and energy, but also is utilized world widely as a source of many naturally occurring and some synthetic chemicals, used in flavorings, drugs, fragrances, dyes, oils, waxes, tannins, resins, rubbers and special polymers [74]. They are either extracted from or produced by conversion of biomass feedstocks. Biomass was the primary source of organic chemicals for human life until the late nineteenth century when fossil fuels took the stage. Before 1900s, fermentation of sugars supplied large amounts of ethanol, butanol and acetone; chars, methanol, acetic acid and acetone were manufactured by pyrolysis of wood [74]. Biomass was then gradually displaced by coal and oil as the feedstock for commodity chemicals. Coal, derived from plants and trees, became the major source of fuels and chemicals at about 1910. Petroleum, derived from organic matter in the ocean, has been the world's most important source of fuels and chemicals since about 1950. It has a high energy density (about 6 GJ/barrel), is easily transported and is relatively abundant. Sophisticated supply and conversion systems have been developed for its use and countless chemicals and polymers and other derivatives are made from petroleum. But, in short, petroleum supplies are finite and are running out; it is found, to a large extent, in politically unstable areas of the world and it is a nonrenewable fossil fuel whose use contributes greatly to global climate change. Recently, as oil and natural gas

costs increase, as well as the environmental concerns, much interest and investment for the manufacture of fuels and chemicals have been reverted to biomass. Research and technology are focusing on developing advanced biomass conversion processes (thermal and microbial) to provide fuels and chemicals at costs that are competitive with those from fossil fuels in a so-called biorefinery.

The biorefinery addresses two goals: on the energy side, displacement of imported petroleum, on the economic side, establishment of a biobased industry [75]. The biorefinery is only competitive to the petroleum refinery when the system is not limited to fuel. Building a biorefinery system based on chemical products can realize a high return on investment and assist industry expansion [76]. Ideally, the biorefinery produces chemicals in the first place and fuels as byproducts [77]. The integration of fuels and chemicals in the biofinery system helps achieve both the energy and economical goals. Analogous to a petrochemical refinery, the biofinery takes the complex raw materials form nature, separates and processes them into simpler building blocks and converts the building blocks into marketplace products. In a general form, a biorefinery supplies carbohydrates (in the form of cellulose, hemicellulose and sugars), aromatics (in the form of lignin, which is a highly cross-linked polymer built of substituted phenols) and hydrocarbons (in the form of plant oils) [75]. Production of chemicals from renewable feedstocks represents a sound and sustainable approach, where the molecules from the biobased resources already contain some functional groups so that the synthesis of derivative chemicals generally requires fewer steps than from hydrocarbons [77]. Synthesis could combine both catalytic and enzymatic steps, adapted to the feedstocks.

This section deals with biomass and the possibility of its conversion to chemicals and to a lesser extent, to fuels. How does biomass measure up as a supply source in relation to petroleum? Huge amounts of biomass, up to 200 Gt/year, are produced around the world, a number to be compared to 7 Gt/year of extracted fossil fuels [1]. Biomass resources are renewable and, unlike fossil fuels, are CO_2 neutral. According to the U.S. roundmap for biomass technologies— 2020 vision goals [1], bio-based chemicals should attain 18% of the U.S. market. This appears to be attainable; biomass conversion to chemicals now involves almost every major industrial company as well as small businesses and government laboratories. The term biomass includes all lignocellulosic material, such as wood and paper mill residues and agricultural plant residues. In 2004, as part of DOE's Biomass Program in the Energy Efficiency & Renewable Energy Offices, scientists started with a list of 300 potential compounds that could be made from lignocellulosic material. A short list of 30 compounds was selected and from among these, a final 12 top-tier compounds were chosen [78]. The 12 value added chemicals that could reasonably be produced from sugars via biological or chemical conversions have 3 to 6 carbon atoms and multiple functional groups with high potential to be converted to new families of compounds. The twelve compounds are shown in the appendix. The twelve building block chemicals fall into two categories: acids and polyols. The polyols are available from sugars and animal fats. These compounds contain multiple functional hydroxyl groups available for diverse organic reactions, such as etherification, polymerization, dehydration, esterification, oxidation and dehydroxylation. The transformation of polyols can provide marketable chemicals as substitutes for those made from petroleum.

There is now great interest in the industrial application of feedstocks from renewable resources because sustainability has become increasingly important for the chemical industry

[79, 80]. Glycerol, one of the twelve "valuable" chemicals, is now commercially obtained as a byproduct in saponification or transesterification of fats and oils to make soap and biodiesel. The expansion of biodiesel production by transesterification of vegetable oils is responsible for the surplus production of glycerol in the market. Consequently, the price of glycerol has dropped dramatically and is expected to be lower than propylene glycol. Finding new outlets for glycerol with high value products would improve the economy of the biodiesel business.

Glycerol is an intermediate in the synthesis of a large number of compounds used in industry [81-83]. We have discussed obtaining hydrogen by aqueous phase reforming of various polyols, with emphasis on glycerol as a source of hydrogen. We have chosen to examine a way of obtaining valuable chemicals from the same polyol, glycerol. The integration of the two processes (chemicals and fuel) will benefit each other and open a new era of biorefinery.

Glycerol is structurally analogous to sugars and sugar alcohols; conversion products developed for glycerol could also be applicable to glucose, sorbitol, xylitol, etc., greatly increasing the diversity of chemicals from biomass. Our perspective to increase the value of glycerol produced in biodiesel plants involves the possible conversion of glycerol into two major commodity chemicals: 1,2- propanediol and 1,3-propanediol. 1,3-Propanediol can be formulated into a variety of industrial products. Its most relevant application has been in the formulation of polymers (polytrimethylene terephthalate, PTT), where 1, 3-propanediol is copolymerised with terephthalic acid ($C_6H_4(COOH)_2$) to produce polyesters, used in the manufacture of carpet and textile fibers with unique properties of chemical resistance, light stability, and dyeability [84, 85]. 1,2-Propanediol is widely used as moisturizers, solvents and lubricants in medicines, cosmetics, food, toothpaste and tobacco products. 1,3-Propanediol is currently produced from

petroleum derived ethylene oxide [86], which reacts with synthesis gas in the presence of cobalt catalyst to form 3-hydroxypropanal ($HOCH_2CH_2CHO$); then hydrogenation of 3-hydroxypropanal produces 1,3-propanediol. 1,2-Propanediol is produced from petroleum derived propylene [87] via propylene oxide which reacts with water to produce 1,2-propanediol. Our aim is to produce both diols by an alternative route via hydrogenolysis of glycerol.

6.2 HYDROGENOLYSIS OF GLYCEROL

Typical diol products of dehydroxylation of glycerol could be 1,2-propanediol, 1,3-propanediol and ethylene glycol, with yields depending on the reaction temperature, pressure and solvent. There have been many researches before on this subject using homogeneous catalysts. Che patented the production of propanediols by reaction of glycerol and synthesis gas in a basic organic solvent in the presence of a tungsten and Group VIII metal-containing catalyst; 1,3-Propanediol and 1,2- propanediol were produced with 20 and 23% yield, respectively [88]. Schlaf et al. described the dehydroxylation of glycerol in sulfolane (2,3,4,5-tetrahydrothiophene-1,1-dioxide, $C_4H_8O_2S$) catalyzed by a homogeneous complex of ruthenium under mild conditions (52 bar, 110 °C) with low yields (<5%) of 1,2-propanediol and 1,3-propanediol [89]. Drent and Jager developed a process for the catalytic hydrogenolysis of glycerol in the presence of a homogenous palladium complex in a water–sulfolane mixture in the presence of methanesulfonic acid. After 10 hours reaction, 1-propanol, 1,2-propanediol and 1,3-propanediol were detected in a 47: 22: 31 ratio [90].

Hydrogenolysis of glycerol using heterogeneous catalysts has also been attempted. Casale and Gomez first reported a method for hydrogenation of glycerol over a sulfide-Ru/C

catalyst in the presence of a base to give oxygenated C1-C3 compounds [91]. Further, they developed a similar process using copper and zinc catalyst; at 270^{o}C and 100 bar of hydrogen a conversion of glycerol of 99.4% with selectivity to 1,2-propanediol of 84.4% was reached [91]. They later patented a process for production of 1,2-propanediol and lactic acid in the presence of ruthenium catalysts modified with sulphides, at a temperature of at least 200^{o}C [92]. Schuster, et.al patented a process for the preparation of 1,2-propanediol by catalytic hydrogenation of glycerol using a catalyst comprising the metals cobalt, copper, manganese and molybdenum with a complete conversion of glycerol and a yield of 1,2-propanediol up to 95% [93]. Hass et al patented a process of simultaneous production of 1,2-propanediol and 1,3-propanediol from glycerol solutions at a temperature of 300^{o}C using two stages, achieving a yield of 60% to 1,3-propanediol and 10% to 1,2-propanediol [94]. Recently, Werpy et al, patented the hydrogenolysis of glycerol over Ni/Re catalyst with yields of 1,2-propanediol, 1,3-propanediol and ethylene glycol to be 44%, 5%, and 13% respectively [95]. Lahr and Shanks studied the influence of reaction conditions and the introduction of small amounts of sulfur to make the catalyst more selective [96]. Suppes and coworkers [97] recently described the selective preparation of 1,2-propanediol under significantly low hydrogen pressure (200 psi). Perosa et al., reported the selective dehydroxylation of glycerol to 1,2-propanediol under 10 bar hydrogen pressure and at 190^{o}C over Raney nickel, without solvent, with maximum conversion and yield of 97 and 71%, respectively [98].

Gallezot et al., studied the effects of solvent and additives on the selectivity of target molecules and reaction rates on the hydrogenolysis of glycerol [99]. Glycerol was hydrogenolyzed at 180^{o}C and 80 bar of hydrogen over supported metal catalysts (Cu, Pd and Rh on ZnO, C and Al_2O_3) in H_2O, sulfolane, and dioxane ($C_4H_8O_2$) with additives (H_2WO_4). They

achieved a maximum selectivity to 1,2-propanediol of 100%, with a yield of 19%, in water over CuO/ZnO catalysts. They observed increases of the selectivity to 1,3-propanediol and yields of 12 and 4%, respectively, at 32% of conversion in sulfolane.

Besides glycerol, sorbitol, a hydrogenation product of glucose, is another polyol candidate for synthesis of valuable chemicals via hydrogenolysis. Gallezot et al., have studied the hydrogenation of glucose to sorbitol on ruthenium and Raney-nickel catalysts [100, 101]. The selectivity to sorbitol was higher than 99.2% at 100% conversion. They also investigated the hydrogenolysis of sorbitol on CuO-ZnO catalysts [102] and achieved a 73% yield of C4+ polyols with a 63% yield of deoxyhexitols, which include C_6 diols, triols, and tetrols. Schuster and Himmele patented a process for lower polyhydric alcohols prepared by catalytic hydrogenolysis of sucrose in an aqueous solution by using a catalyst consists of cobalt, copper manganese and achieved butane-1,2-diol and hexane-1,2,5,6-tetrol in low yields [103]. Saxena et al., found that a multicomponent (Ni, Mo and Cu) catalyst had high activity for the hydrogenolysis of sucrose to produce industrially important glycerol, ethylene glycol, propylene glycol, and sorbitol [104].

Most catalysts involved in hydrogenolysis of glycerol and other polyols were multicomponent catalysts, which increases cost and probability of catalysts deactivation. It is our intent to develop a simple metal catalyst with high activity and selectivity for target glycols, and to investigate the optimum operation conditions to achieve high yield of propylene glycol.

6.3 EXPERIMENTAL METHODS

6.3.1 Catalyst preparation

Zirconia-supported copper catalysts were prepared by incipient wetness impregnation methods. The precursor for deposition of Cu on zirconia was copper (II) nitrate ($Cu(NO_3)_2*3H_2O$). A solution of Cu salt was added dropwise to the $Zr(OH)_4$ while stirring, followed by drying in an oven at 110^oC for overnight. The catalysts were calcined in air at 350^oC for 3 hours.

6.3.2 Experimental setup

Hydrogenolysis of glycerol was carried out in an autoclave reactor. The system consists of a horizontal shaking 40ml microautoclave and a temperature controlled sand bath. After 1 gram of catalyst and 15 ml of glycerol solution were loaded, the reactor was purged with helium and pressurized to 2000 psi at room temperature to test for leaks. After release of helium, the reactor was flushed with hydrogen to remove air and helium and then pressurized to 1500 psi at room temperature before immersing into a fluidized sand bath and heated to the final reaction temperature of 250^oC. The reactor was shaken horizontally at 180 cycles per minute. The reaction was terminated by removal from the sand bath and immediately cooled with running cold water. The liquid product was collected and analyzed by GC (5890).

6.3.3 Product analysis

The properties of hydroxyl compounds depend largely on the presence of active hydrogen atoms in the molecule. Polar O-H groups that can undergo hydrogen bonding contribute significantly to intermolecular attraction manifested in the high melting and boiling points of the compounds [105]. Gas chromatographic separation of polyhydroxyl compounds is difficult because these substances are not sufficiently volatile for analysis by gas chromatography (GC) [106]; polyols with four or more hydroxyl groups are difficult to analyze directly by GC. Small polyols such as ethylene glycol and glycerol show broad nonsymmetrical peaks on chromatograms, leading to poor detection limits and reproducibility.

A general way to avoid these problems is based on the conversion of hydroxyl compounds to thermally stable volatile derivatives. The principle is to replace active hydrogen by certain functional groups, such as trimethylsilyl groups, to reduce the polarity of the compound and decrease the possibilities of hydrogen bonding. Compound stability is enhanced by reduction in the number of reactive sites with active hydrogen [107]. Silylation is an important tool in both analytical and synthetic chemistry. The term "silyl" is generally applied to the trimethylsilyl group, $-Si(CH_3)_3$, abbreviated TMS.

$$R(OH)_n + n\,XSi(CH_3)_3 \rightarrow R(OTMS)_n + n\,XH \qquad (6.1)$$

Generally all molecules with active hydrogen can be converted to their trimethylsilyl ethers [107]. This method has been used since the late fifties in gas chromatography and mass spectrometry for the derivatization of a wide variety of products and functional groups [108-113]. The advantage of using trimethylsilyl ethers for gas chromatography was noted in 1958 by Wender, Langer and Pantages [114]. In 1963 Sweeley et al reported application of hexamethyldisilazane (HMDS, $[((CH_3)_3Si)_2NH]$) and trimethylchlorosilane (TMCS, $(CH_3)_3ClSi$)

in pyridine for sugar compound for gas chromatography [115]; the procedure published in this paper was classic in this field and influenced the development of conversion of hydroxyl substituted compounds to their TMS ethers.

HMDS is one of the original reagents used to prepare TMS derivatives. Although, it is not the strongest TMS donor among the reagents, it reacts more selectively than stronger silylating agents; its power can be increased by catalysts (mostly acidic); it can be used without solvent [116].

Both trimethylsilyl groups in HMDS are available so that the stoichmetric ratio is one mole of HMDS for two moles of hydroxyl groups. The reagent is normally used in excess, usually more than 3 times, with a catalyst, such as TMCS [107]. Trifluoroacetic acid (TFA), CF_3COOH, is an effective catalyst for silylation of carbohydrates [117, 118].

We have used a simple procedure which uses very small amounts of sample and reagent and takes a short time. The procedure is described here: place 60 mg of sample (e.g. 1wt% glycerol in water solution) in a reaction vial followed by addition in 2 ml pyridine as a solvent and 2 ml HMDS and mixing. Carefully add 0.2 ml trifluoroacetic acid, which is used as a catalyst, followed by vigorous shaking about 1min. Heat for the reaction is provided by the acid-base reaction of pyridine and trifluoroacetic acid. Allow the mixture to stand for 15 min and then analyze by gas chromatography. The small amounts of water present in the sample react with HMDS to form siloxane $((CH_3)_3Si)_2O$, which comes early in the gas chromatograph and can be differentiated from glycerol silylation products.

6.3.4 Results and discussion

Hydrogenolysis of 10 wt% of glycerol in water solution over 20wt% Cu/ZrO_2 catalyst at 250°C and 1500psi initial hydrogen pressure gave propylene glycol (1,2-propanediol) as the major product. 1,3-Propanediol was not detected in the liquid product. GCMS indicated that there were small amounts of ethylene glycol and acetol (CH_2OHCHO) in the liquid product.

Figure 25 shows the glycerol conversion and propylene glycol selectivity as well as yield. For each data point, conversion of glycerol, selectivity and yield of 1,2-propanediol were calculated from analysis data. Conversion of glycerol is defined as the ratio of number of moles of glycerol consumed in the reaction to the total moles of glycerol initially present. Yield of propylene glycol is defined as the ratio of the number of moles of propylene glycol produced in the hydrogenolysis to the theoretical number of moles of propylene glycol that could be produced from the reaction. Selectivity of propylene glycol is calculated from yield and conversion.

$$\text{Glycerol conversion} = \frac{\text{Moles of glycerol consumed}}{\text{Total moles of glycerol initially present}} \times 100\% \quad (6.2)$$

$$\text{Propylene glycol yield} = \frac{\text{Moles of propylene glycol produced}}{\text{Total moles of glycerol initially present}} \times 100\% \quad (6.3)$$

The Cu/ZrO_2 catalyst is highly active for dehydroxylation of glycerol to propylene glycol. Initial concentration of glycerol was 10 wt% (0.2 mole%). Glycerol conversion increased with time; over 50% of glycerol was converted after 5 hours reaction and conversion of glycerol increased to near 90% at 19 hours. The propylene glycol selectivity slightly decreased with time; 87% of 1,2-propanediol selectivity was achieved after 5 hours and close to

70% was achieved at 19 hours. The yield of propylene glycol increased from 48% at 5 hours to 59% at 19 hours. No deactivation of the catalyst was observed. The base shaking frequency was 180 rpm, we also tested at 300 rpm. No difference in the reaction rate (referring to glycerol conversion) was found between the two mixing levels, which indicated no external diffusion was occurring under the experimental conditions. Hydrogenolysis of glycerol over Cu/ZrO_2 catalyst did not give good yields of 1,3-propanediol. It has been, however, reported that 1,3-propanediol can be obtained in good yields by fermentation of glycerol using anaerobic bacteria [119, 120]. Dupont and Tate & Lyle are building plants to make 1,3-propanediol from glycerol by enzyme fermentation [121].

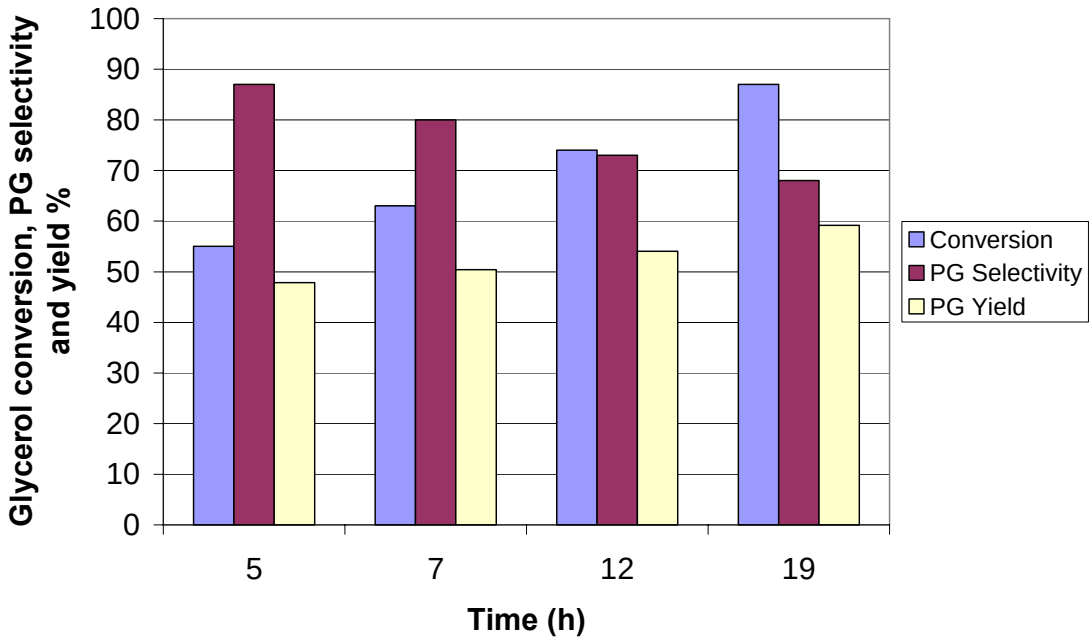


Figure 25. Experimental data from hydrogenolysis of glycerol (10 wt%) at 250^{o}C and 1500psi hydrogen pressure

6.3.4.1 Effect of reaction temperature

Temperature has a significant effect on the conversion of glycerol and yield of 1,2-propanediol. Hydrogenolysis of glycerol (10 wt%) were carried out at 200, 220 and 250^{o}C at a hydrogen pressure of 1500psi over 20 wt% Cu/ZrO_2 catalyst, each for 6 hours. Table 16 shows the effect of reaction temperature on the glycerol conversion and yield of propylene glycol. As the reaction temperature increased from 200 to 250^{o}C, the conversion of glycerol increased from 21% to 60%; the yield of 1,2-propanediol increased from 18% to 50%, while the selectivity of 1,2-propanediol slightly decreased from 88% to 83%. At initial hydrogen pressure of 1500 psi, high temperatures (above 200^{o}C) lead to high activity of the Cu/ZrO_2 catalyst. Due to safety concerns, we did not increase the reaction temperature above 250^{o}C, however literature [97] shows that selectivity and yield of 1,2-propanediol may decrease at temperatures above 250^{o}C, due to excessive hydrogenolysis, converting propanediols to lower alcohols.

Table 16. Effect of temperature on glycerol conversion and 1,2-propanediol yield and selectivity from hydrogenolysis

Temperature (^{o}C)	Conversion %	1,2-propanediol Yield %	1,2-propanediol Selectivity %
200	21	18	88
220	32	25	79
250	60	50	83

*Hydrogenolysis of 10wt% glycerol at 200, 220 and 250^{o}C, at a hydrogen pressure of 1500psi over 20 wt% Cu/ZrO_2 catalyst, each for 6 hours.

6.3.4.2 Effect of reaction pressure

The hydrogenolysis of 10 wt% glycerol solution at different hydrogen pressures (800, 1200 and 1500psi) at a constant temperature of 250^{o}C was performed to determine the effect of initial hydrogen pressure on the overall reaction. Table 17 provides the summary of experimental results (after 6 hours) of glycerol conversion, 1,2-propanediol selectivity and yield at each reaction condition. As the initial hydrogen pressure increased from 800 to 1500psi, the conversion of glycerol increased from 25 to 60%, and selectivity of 1,2-propanediol increased from 60 to 83%; the increase in yield was from 15 to 50%. It is clear that higher hydrogen pressure leads to higher conversion of glycerol and better selectivity and yield of 1,2-propanediol.

Table 17. Effect of hydrogen pressure on glycerol conversion and 1,2-propanediol yield and selectivity from hydrogenolysis

Pressure (psi)	Conversion %	1,2-propanediol Yield %	1,2-propanediol Selectivity %
800	25	15	60
1200	42	32	75
1500	60	50	83

*Hydrogenolysis of 10wt% glycerol at 250^{o}C and at different hydrogen pressure (800, 1200 and 1500psi) over 20 wt% Cu/ZrO_2 catalyst, each for 6 hours

6.3.4.3 Effect of feed concentration

Water is not only a solvent but also a product of the hydrogenolysis of glycerol. Ideally, it is preferable to use a concentrated feed in order to reduce the energy cost of heating water and to increase reactor efficiency (reactor space time). Removal of water from the product drives the hydrogenolysis reaction forward. Therefore we carried out the hydrogenolysis of glycerol with different concentrations (10%, 25% and 40% of glycerol in water solution). Table 18 shows that increasing glycerol concentration from 10 to 25% only slightly drops the yield and selectivity of 1,2-propanediol; a larger decrease is observed when the water content decreases from 75 to 60%, so that the glycerol conversion drops from 55 to 34% and the 1,2-propanediol yield drops from 44 to 26%. Dilute feed solutions favor high yields of 1,2-propanediol and high conversions of glycerol.

Table 18. Effect of water content on glycerol conversion and 1,2-propanediol yield and selectivity from hydrogenolysis

Glycerol concentration %	Conversion %	1,2-propanediol Yield %	1,2-propanediol Selectivity %
10	60	50	83
25	55	44	80
40	34	26	75

*Hydrogenolysis of different concentrations of glycerol (10%, 25% and 40%) at 250^{o}C, at 1500psi hydrogen pressure over 20 wt% Cu/ZrO_2 catalyst, each for 6 hours

6.3.4.4 Effect of metal loading

Copper catalysts are more effective in hydrogenolysis of C-O bonds rather than C-C bonds, so they are useful in catalyzing C-O bond breakage in hydrogenolysis, preserving the carbon chain structure in polyols to make useful chemicals [47, 122]. We prepared a series of Cu/ZrO_2 catalysts with copper loadings from 5 to 25 wt% by incipient impregnation. Table 19 shows reaction results of glycerol hydrogenolysis on copper catalysts with various loadings. The conversion of glycerol and the yield of 1,2-propanediol increased with copper loading from 5 to 20 wt%. Further increase to 25 wt% resulted in a decline in activity due to coalescence of copper particles at higher copper loading.

Table 19. Effect of metal loading on glycerol conversion and 1,2-propanediol yield from hydrogenolysis

Cu loading (wt%)	Glycerol conversion (%)	1,2-propanediol yield (%)
5	32	24
15	48	40
20	60	50
25	50	38

*Hydrogenolysis of 10 wt%glycerol at 250^{o}C, at 1500psi hydrogen pressure over Cu/ZrO_2 with Cu loading ranges from 5 to 20%, each for 6 hours

As shown in Figure 26 (temperature programmed reduction, TPR), when the copper loading is low, i.e. 5 wt% and 10 wt%, only one peak at about 170°C is observed. This peak represents the reduction of small copper particles dispersed on the ZrO_2 support. When the copper loading is higher than 15 wt%, another peak appears at about 200°C. This peak represents the reduction of large copper particles, indicating the coalescence of copper particle and decreasing copper surface area, hence, leading to a decrease in activity when copper loading exceeds 20 wt%.

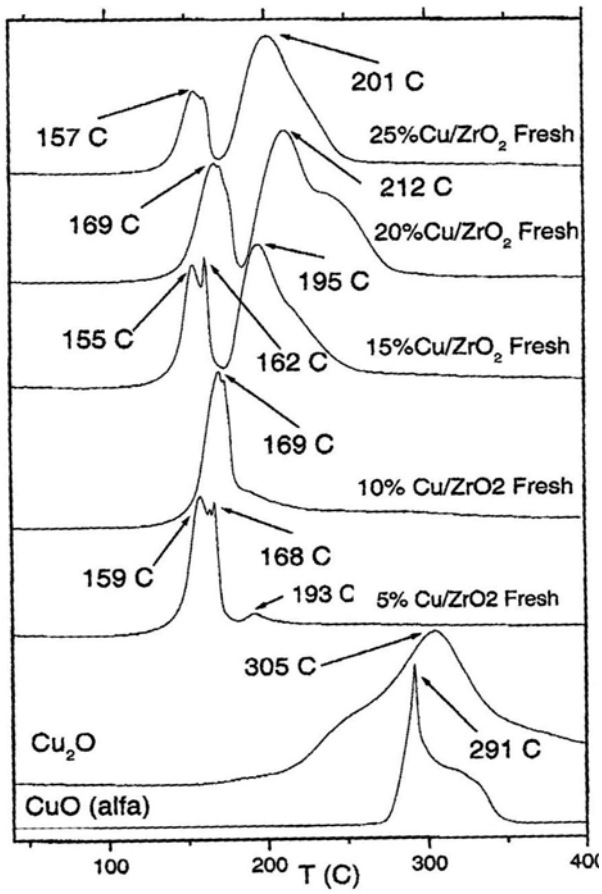


Figure 26. TPR image of the Cu/ZrO_2 catalyst

6.4 CONCLUSIONS

Hydrogenolysis of glycerol to produce value-added chemicals such as 1,2-propanediol was investigated using a simple Cu/ZrO_2 catalyst. Cu/ZrO_2 catalysts showed high activity and selectivity for the target product (1,2-propanediol), better than some of the multicomponent catalysts and easier to separate from products than the homogeneous catalysts in the literature . More than 80% conversion of glycerol and close to 60% yield of 1,2-propanediol were achieved at 250^{o}C and 1500psi hydrogen pressure. We studied the optimum operation conditions and found that high temperature and high hydrogen pressure favors the hydrogenolysis of glycerol to 1,2-propanediol. We chose 250^{o}C and 1500psi hydrogen pressure as the optimum condition for safety consideration. The diluted glycerol gave higher conversions of glycerol and yields of 1,2-propanediol than the concentrated feed solution. High Cu loadings might lead to coalescence of copper particle and decreasing copper surface area, which can cause catalyst deactivation, as shown from the 25% Cu/ZrO_2 catalyst. The hydrogenolysis of glycerol provides an alternative route to produce a renewable chemical usually made from petroleum.

APPENDIX A

A1 SAMPLE CALCULATION

Calculation of hydrogen turnover frequency (TOF)

Hydrogen turnover frequency is defined as the number of hydrogen molecules produced per active site per unit time. TOF calculation is based on hydrogen volumetric rate from experimental data and metal dispersion results from catalyst chemisorption test.

- Take aqueous phase reforming of 10 wt% ethylene glycol in water solution over 1 gram Pt/Al_2O_3 (1 wt% Pt) catalyst as an example.

  Hydrogen volumetric rate at 220^{o}C is 8.1 ml/min; data is in Appendix Table 20,

  Pt/Al_2O_3 (1 wt% Pt) catalyst has a 56.3% metal dispersion; data is in Table 12

  Pt molecular weight is 195 gram/mol;

  H_2 TOF is calculated as

$$8.1 \text{ (ml/min)} \div 22400 \text{ (ml/mol)} \div (1 \text{ gram} \times 1\% \times 56.3\% \div 195.08 \text{ g/mol}) = 12.6 \text{ min}^{-1}$$

- Take aqueous phase reforming of 10 wt% glycerol in water solution over 1 gram Pt/Al_2O_3 (1 wt% Pt) catalyst as an example

  Hydrogen volumetric rate at 220^oC is 4.0 ml/min; data is in Appendix Table 20,

  Pt/Al_2O_3 (1 wt% Pt) catalyst has a 56.3% metal dispersion; data is in Table 12

  Pt molecular weight is 195 gram/mol;

  H_2 TOF is calculated as

$$4.0 \text{ (ml/min)} \div 22400 \text{ (ml/mol)} \div (1 \text{ gram} \times 1\% \times 56.3\% \div 195.08 \text{ g/mol}) = 6.2 \text{ min}^{-1}$$

A2 REPRODUCIBILITY OF EXPERIMENTAL DATA

Table 20. Duplicate runs of aqueous phase reforming of 10 wt% glycerol over 1 wt% Pt Pt/Al_2O_3 catalyst

Run No.	Cat.	Reaction conditions				H_2 rate ml/min
		Feed	Feed rate ml/min	P, psi	T,^oC	
Gll009	Pt/Al_2O_3 1wt% Pt	10 wt% glycerol in water	0.1	385	220	4.0
				980	280	11.0
Gll007	Pt/Al_2O_3 1wt% Pt	10 wt% glycerol in water	0.1	385	220	4.5
				980	280	11.2

*Duplicate runs show experimental error is within 12.5% for APR of 10 wt% of glycerol over 1 wt% Pt Pt/Al_2O_3 catalyst

APPENDIX B

EXPERIMENTAL RESULTS

Table 21. Experimental results from aqueous phase reforming of different polyols

Run No.	Cat.	Reaction conditions				Results							
		Feed	Feed rate ml/min	P, psi	T,°C	H_2 %	CO_2%	CH_4%	C_2H_6%	C_3H_8%	H_2 rate ml/min	H_2 selectivity %	Alkane selectivity%
EG002	Pt/Al_2O_3 1wt% Pt	10 wt% ethylene glycol in water	0.1	385	220	70.1	29.5	0.3	0.2	N/A	8.1	93.1	2.0
				625	250	68.3	31.0	0.5	0.2	N/A	15.4	85.7	2.9
Gll009	Pt/Al_2O_3 1wt% Pt	10 wt% glycerol in water	0.1	385	220	61.7	34.3	3.7	0.3	0.03	4.0	68.3	11.3
				625	250	61.9	34.3	3.4	0.4	0.05	7.8	68.6	11.3

Table 21. (Continued)

Run No.	Cat.	Reaction conditions				Results							
		Feed	Feed rate ml/min	P,psi	T,°C	H_2 %	CO_2%	CH_4%	C_2H_6%	C_3H_8%	H_2 rate ml/min	H_2 selectivity%	Alkane selectivity%
Sorbi025	Pt/Al_2O_3 5wt% Pt	1wt% sorbitol in water	0.1	385	220	59.7	35.8	3.5	0.8	0.2	1.2	66.3	13.9
				625	250	57.2	36.9	4.1	1.3	0.5	1.1	58.5	18.3
Manni025	Pt/Al_2O_3 5wt% Pt	1wt% mannitol in water	0.1	350	220	59.5	37.0	2.6	0.7	0.2	1.3	65.9	11.1
				625	250	56.2	38.2	4.0	1.2	0.4	1.0	56.5	16.8

Table 21. (Continued)

Run No.	Cat.	Reaction conditions				Results							
		Feed	Feed rate ml/min	P,psi	T,°C	H_2 %	CO_2%	CH_4%	C_2H_6%	C_3H_8%	H_2 rate ml/min	H_2 selectivity %	Alkane selectivity%
Glucose26	Pt/Al_2O_3 5wt% Pt	1wt% glucose in water	0.1	385	220	52.1	42.6	3.5	1.1	0.6	0.9	52.2	14.9
				625	250	25.1	73.6	0.6	0.2	0.5	0.2	16.4	3.4
Corn024	Pt/Al_2O_3 5wt% Pt	1wt% corn syrup in water	0.1	385	220	14.1	83.1	1.7	0.6	0.4	0.03	8.1	4.9
				625	250	10.4	86.1	1.6	0.6	1.3	0.04	5.6	7.1

Table 21. (Continued)

Run No.	Cat.	Reaction conditions				Results							
		Feed	Feed rate ml/min	P,psi	T,°C	H_2 %	CO_2%	CH_4%	C_2H_6%	C_3H_8%	H_2 rate ml/min	H_2 selectivity %	Alkane selectivity%
Suc002	Pt/Al_2O_3 1wt% Pt	1wt% sucrose in water	0.1	385	220	51.9	37.4	8.0	1.5	1.2	1.5	62.4	28.0
				625	250	41.2	46.5	6.7	1.5	4.1	0.6	34.5	32.1
Sugar023	Pt/Al_2O_3 5wt% Pt	1wt% table sugar in water	0.1	385	220	58.3	34.8	4.8	1.2	0.9	1.1	66.6	17.7
				625	250	50.0	40.1	5.1	1.0	4.1	0.5	42.4	32.2

*Hydrogen production rates were measured at each temperature and pressure before taking liquid sample for analysis

*Gas products concentration was measured by GC at the same time when hydrogen rates were measured

*Selectivity of hydrogen and alkane were calculated by gas products concentration and described in Chapter 5

Table 22. Experimental results from aqueous phase reforming of glycerol over alumina supported catalysts

Run No.	Cat.	Reaction conditions				Results						
		Feed	Feed rate ml/min	P, psi	T,°C	H_2 %	CO_2%	CH_4%	CO %	H_2 rate ml/min	H_2 selectivity %	Alkane selectivity%
Gll019	Ru/Al_2O_3 5wt% Ru	10 wt% glycerol in water	0.1	625	250	15.4	36.7	46.8	0	1.6	7.6	57.6
Gll020	Pd/Al_2O_3 5 wt% Pd	10 wt% glycerol in water	0.1	625	250	47.5	19.0	8.3	25.2	2.2	38.7	11.2

Table 23. Experimental results from aqueous phase reforming of glycerol over Pt catalysts with different metal loadings

Run No.	Cat.	Reaction conditions				Results							
		Feed	Feed rate ml/min	P,psi	T,^{o}C	H_2 %	CO_2%	CH_4%	C_2H_6%	C_3H_8%	H_2 rate ml/min	H_2 selectivity %	Alkane selectivity%
Gll010	Pt/Al_2O_3 5wt% Pt	10 wt% glycerol in water	0.1	625	250	61.2	33.1	4.8	0.5	0.1	15.8	66.4	15.7
Gll011	Pt/Al_2O_3 0.3 wt% Pt	10 wt% glycerol in water	0.1	625	250	60.7	34.3	4.7	0.3	0.05	2.4	68.6	11.3

Table 24. Experimental results from aqueous phase reforming of glycerol over Pt catalysts

Run No.	Catalyst	Feed	Gas production rate (ml/min)	220°C			250°C			280°C		
				Time(h)								
Gll022	Pt/Al_2O_3 With 1wt% Pt	10 wt% glycerol 0.1 ml/min		3.5	6	10.5	13.5	17	21	25	27	32
			H_2	1.2	3.6	4	6	7.4	7.8	9.4	10.8	11.2
			CO_2	0.7	1.7	2.1	2.5	3.6	4.3	4.6	4.9	5.8
			CH_4	0.05	0.1	0.3	0.3	0.37	0.5	0.5	0.5	0.7
Gll022	Pt/SiO_2 With 1wt% Pt	10 wt% glycerol 0.1 ml/min	Gas production rate (ml/min)	220°C			250°C			280°C		
				Time(h)								
				3	6	9	12	16	20	24	26.5	32
			H_2	0.1	0.4	1.2	2.5	3	3.7	3.9	3.9	4
			CO_2	0.03	0.1	0.5	1.3	1.8	2.1	2.2	2.4	2.4
			CH_4	0.003	0.009	0.01	0.05	0.1	0.14	0.17	0.22	0.3

Table 24. (Continued)

Run No.	Catalyst	Feed	Gas production rate (ml/min)	220°C			250°C			280°C		
				Time(h)								
Gll022	Pt/MgO With 1wt% Pt	10 wt% glycerol 0.1 ml/min		3.5	7	10	14	16.5	21	24	28	30
			H_2	0.2	0.8	1.5	1.7	1.9	2.6	2.7	2.8	3.4
			CO_2	0.09	0.2	0.8	0.9	1	1.5	1.7	1.9	2
			CH_4	0.01	0.07	0.1	0.1	0.12	0.2	0.3	0.3	0.34
Gll022	Pt/TiO_2 With 1wt% Pt	10 wt% glycerol 0.1 ml/min	Gas production rate (ml/min)	220°C			250°C			280°C		
				Time(h)								
				3	7	11	14	17	20	24	27	31
			H_2	0.4	0.7	1.2	1.4	1.7	2.3	2.4	2.8	3.2
			CO_2	0. 3	0.5	1.0	1.1	1.4	2.1	2.3	2.4	2.7
			CH_4	0.02	0.08	0.16	0.19	0.22	0.28	0.3	0.34	0.5
Gll022	Pt/ZrO_2 With 1wt% Pt	10 wt% glycerol 0.1 ml/min	Gas production rate (ml/min)	220°C			250°C			280°C		
				Time(h)								
				3.5	7	10	14	16.5	21	24	28	30
			H_2	0.1	0.24	0.3	0.33	0.4	0.31	0.22	0.12	0.09
			CO_2	0.03	0.11	0.16	0.17	0.25	0.25	0.21	0.09	0.03
			CH_4	0.008	0.01	0.02	0.02	0.03	0.03	0.02	0.02	0.01

Table 25. Experimental results from aqueous phase reforming of selected oxygenated hydrocarbons

Run No.	Cat.	Reaction conditions				Gas products compostion			
		Feed	Feed rate ml/min	P, psi	T,°C	H_2 %	CO_2%	Alkane %	H_2 rate ml/min
13Pro011	Pt/Al_2O_3 1wt% Pt	1,3-propanediol in water 10 wt%	0.1	850	270	46.5	32.6	20.9	3.4
12Pro013	Pt/Al_2O_3 1wt% Pt	1,2-propanediol in water 10 wt%	0.1	850	270	58.9	30.7	10.4	4.1
1Prop014	Pt/Al_2O_3 1wt% Pt	1-propanol in water 10 wt%	0.1	850	270	45.4	26.6	28.0	3.2
PEG001	Pt/Al_2O_3 1wt% Pt	PEG 200 in water 10 wt%	0.1	385	220	-	-	-	1.1
				625	250	-	-	-	2.5

Table 26. Reforming of ethylene glycol and PEG in a batch system

Run No.	Cat.	Reaction conditions					Gas product composition		
		Reactant	Volume ml	ΔP, psi	T,°C	Time h	H_2 %	CO_2%	Alkane %
EGB001	Pt/Al_2O_3 1wt% Pt	10 wt% ethylene glycol in water	15	166	250	8	79.6	32.6	20.9
PEGB002	Pt/Al_2O_3 1wt% Pt	10 wt% polyethylene glycol in water	15	120	270	7	58.9	30.7	10.4

Table 27. Effect of temperature on H_2 production from aqueous phase reforming of ethylene glycol and from glycerol over 1 wt% Pt/Al_2O_3 catalyst at low flowrate

Catalyst	Feed	Feed rate ml/min	P, psi	T,°C	H_2 rate ml/min	H_2 TOF (1/min)
Pt/Al_2O_3 1wt% Pt	Glycerol in water 1 wt%	0.01	385	220	0.26	0.41
			625	250	0.44	0.68
			980	280	0.64	0.99
	Ethylene glycol in water 1wt%	0.01	385	220	0.45	0.7
			6525	250	0.59	0.91
			980	280	0.77	1.2

Table 28. Effect of pressure on H_2 from aqueous phase reforming of glycerol over 1 wt% Pt/Al_2O_3 catalyst at low flowrate

Catalyst	Feed	Feed rate ml/min	T,^oC	P, psi	H_2 rate ml/min	H_2 TOF (1/min)
Pt/Al_2O_3 1wt% Pt	Glycerol in water 1 wt%	0.01	220	350	0.26	0.41
				400	0.23	0.36
				450	0.19	0.3
				500	0.16	0.26
				600	0.13	0.2

Table 29. Effect of feed concentration on H_2 from aqueous phase reforming of glycerol over 1 wt% Pt/Al_2O_3 catalyst at low flowrate

Catalyst	Feed rate ml/min	P, psi	T,°C	Feed concentration wt%	H_2 rate ml/min	H_2 TOF (1/min)
Pt/Al_2O_3 1wt% Pt	0.01	385	220	1	0.26	0.41
				5	0.44	0.7
				10	0.57	0.9

Table 30. Results of hydrogenolysis of glycerol over 20wt% Cu/ZrO_2 catalyst at 250^oC and 1500 psi initial hydrogen pressure

Time (h)	Glycerol conversion %	1,2-Propanediol selectivity %	1,2-Propanediol yield%
5	55	88	48
7	63	80	50
12	74	73	54
19	87	68	59

APPENDIX C

CATALYST PREPARATION AND CHARACTERIZATION

Table 31. Ratio of water to support used in preparing catalysts by incipient wetness impregnation technique

Support	Water: Support
γ-Al_2O_3	1 ml H_2O: 1.25 g Al_2O_3
TiO_2	1 ml H_2O: 0.5 g TiO_2
MgO	1 ml H_2O: 1.25 g MgO
SiO_2	1 ml H_2O: 0.3 g SiO_2
ZrO_2	1 ml H_2O: 2.2 g ZrO_2

Table 32. BET surface area of Pt catalysts on different supports

Support	BET surface area m_2/ g cat
SiO_2	294
ZrO_2	138
Al_2O_3	133
MgO	59.1
TiO_2	56.8

* 1 wt% Pt loaded onto the supports by a wet incipient impregnation method

APPENDIX D

BUILDING BLOCK CHEMICALS FROM BIOMASS

Table 33. Top 12 building block chemicals

Top 12 building block chemicals
1,4-Diacid (succinic acid, fumaric acid, malic acid)
2,5-Furandicarboxylic acid
3-Hydroxy propionic acid
Aspartic acid
Itaconic acid
Levulinic acid
3-Hydroxybutyrolactone
Glycerol
Sorbitol
Xylitol

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